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Cell model of a fluid with hard-core repulsive long-range attractive potential

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First Reader

Second Reader

Third Reader
CELL MODEL OF A FLUID WITH HARD-CORE
REPULSIVE LONG-RANGE ATTRACTIVE POTENTIAL

An Abstract of a Dissertation
Presented to
the Faculty of the Graduate School
University of Missouri at Rolla

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Ralph Gunther Tross
January 1968
A model of a one-dimensional fluid is investigated in which the particles are embedded in a cellular space grid and interact with a modified Lennard-Jones potential. It is shown that with an appropriate change in the potential function the model is also suitable for a two- or three-dimensional fluid with more restricted interactions. The many-fermion-like nature of the system resulting from the hard-rod repulsive part of the modified Lennard-Jones potential makes possible an isomorphism between occupation numbers (number operators) and spin states (spin operators) of an Ising ferromagnet, permitting a convenient mathematical formulation of the problem in terms of the Ising model formalism. While the spinor-algebraic method of Onsager and Kaufman is seen not to lead to a solution of this problem, a method is found for linearizing the partition function which results in a useful series solution. The validity of the solution is first proved by applying it to a one-dimensional model with nearest-neighbor interactions for which the exact partition function is known in closed form. The series solution is shown to offer a convenient and unified method for obtaining, algebraically, correct low-temperature expansions of the partition function for two- and three-dimensional fluids with nearest-neighbor interactions and similar potentials incorporating only a limited number of bonds. Application of the solution to several infinite systems produces consistent and realistic results in various limits and leads to a correct
picture of a phase transition under certain conditions without recourse to the Maxwell construction. A numerical evaluation and analysis of the series solution, by means of high-speed computer, for small one-, two-, and three-dimensional systems shows realistic thermodynamic behavior and confirms other estimates of the critical temperature of the three-dimensional system.
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CHAPTER I
INTRODUCTION

It is well-known that the molecular theory of the liquid state poses a much more difficult problem than the corresponding theories of the gaseous or solid states. All three theories are, of course, obliged to deal with the immense difficulties of solving a general N-body problem, and all three are likewise hampered by the comparative lack of knowledge concerning the details of intermolecular interactions. However, in the gaseous state the problem can be made amenable to statistical treatment by exploiting the comparatively low density of that state. This approach then leads to the well-known cluster expansions and similar techniques for finding a good approximation to the partition function.\(^1,2,3\) In solids, on the other hand, molecules vibrate about fixed lattice positions, to a very good approximation, so that one can use the periodicity and symmetry of the lattice to reduce the very high multiplicity of the phase integrals involved. In both cases, however, one is obliged to supplement the limited information on molecular interactions that is available by empirical or semiempirical data.

In the liquid state the simplifications applicable to solids and gases are not available. Densities approach those of solids, while the symmetries found in the solid state are lacking. This imposes severe restrictions which make it difficult to find solutions valid in this state. Nor is it possible by and large to extend solutions valid for gases into the liquid region. The cluster expansions mentioned earlier
afford a typical example. It is well-known that these expansions converge absolutely for gases; indeed convergence is quite rapid for dilute gases. One can show readily that this expansion is equivalent to an expansion of the logarithm of the partition function in powers of the activity, \( y \). The radius of convergence of this series is determined by the location of the zeros of the partition function with respect to the origin in the complex \( y \)-plane. Yang and Lee have established a clear connection between these zeros and phase transitions (cf. Chapter V below). For the usual type of Lennard-Jones potential used in this study, the zeros lie on the unit circle in the \( y \)-plane. Since the dilute gas region corresponds to the inside of the unit circle, the cluster expansion converges only in the open region interior to the unit circle and no longer converges in any neighborhood including the zero on the real axis corresponding to the phase transition of interest. Furthermore, since the zeros form a solid wall on the unit circle in the thermodynamic limit (\( \lim_{N \to \infty} \frac{1}{N} \ln Q \) is a lacunary function, cf. ref. 6) it is impossible to extend the cluster expansion analytically into the condensed region which is the region exterior to the unit circle.

The example just cited is typical. Liquid theory has therefore followed its own somewhat different route. By and large the objective is the determination of pair distribution functions from which the thermodynamics of the system may be derived. These functions are usually obtained either from an integral equation like those of Yvon, Born, and Green or Kirkwood, or from some sort of model such as that of Lennard-Jones and Devonshire. An alternative approach that has come to the fore in recent years with the advent of fast computers
is the numerical solution of the problem by such techniques as the Monte Carlo method. These methods have various obvious limitations. The numerical computations give only approximations and do not yield an analytical solution. The integral equation method, on the other hand, leads to complex equations which generally force recourse to something like the Kirkwood superposition approximation to make them tractable. The models have perhaps been the most successful, although frequently symmetries are introduced that are not in keeping with the characteristics of the liquid state.

The present study addresses itself to the problem of a fluid comprised of simple particles, e.g. the molecules of a noble gas. It is assumed that the system is essentially classical. Every particle of the fluid interacts with every other one by means of a modified Lennard-Jones potential. In view of the difficulties outlined above, it is apparent that some simplification is necessary if the problem is to be tractable. Accordingly, consideration is limited initially to a one-dimensional system with all interactions active. Such a system will be found to possess interesting and surprisingly realistic thermodynamic properties. It will be shown that two- and three-dimensional systems with more limited interactions (e.g. nearest-neighbor, next-nearest-neighbor, etc. interactions) can be considered as subsets of the more general one-dimensional model so that the thermodynamics of these systems can be obtained from the one-dimensional solution by an appropriate change in the potential function.

In seeking a suitable mathematical framework in which to couch this problem, one of the considerations was that the solution should hold at all densities and in the liquid-vapor transition region as well. This suggested use of the Ising model, since to this day the Onsager solution
of the two-dimensional Ising problem remains the only exact solution of cooperative phenomena.\textsuperscript{11,12} Accordingly a cellular model was adopted to which the Ising formalism could be applied. The cells provide merely a space grid within which the fluid moves. They are not indicative of any spurious symmetry in the system, but serve only as reference points, breaking up the space accessible to the fluid into a convenient number of discrete elements. The hard-core repulsive part of the modified Lennard-Jones potential used throughout most of this study made it desirable to let the cell size coincide with the effective particle diameter. This naturally restricts cell occupancy to one particle or none and permits an isomorphism to be established between occupation number (number operator) and the spin states (spin operators) of an Ising ferromagnet, which allows a mathematically convenient formulation of the problem in terms of the Ising formalism.

The Ising model, which is basic to the present study, was first investigated by one of Lenz's students, Ernst Ising in 1920.\textsuperscript{13} Since the one-dimensional ferromagnet with nearest-neighbor interactions investigated by him proved not to exhibit any permanent magnetization, the model fell into disuse. Interest in it was revived in the mid-1930's by Peierls in connection with his investigation of more general order-disorder phenomena.\textsuperscript{14} Peierls succeeded in proving that the two-dimensional Ising ferromagnet undergoes a phase transition at sufficiently low temperatures. Van der Waerden, Kramers, and Wannier were able to predict the Curie temperature of such a system shortly thereafter.\textsuperscript{15,16} Interest in the model reached a peak with Onsager's brilliant exact solution of the two-dimensional Ising problem (with nearest-neighbor interactions) and has continued unabated ever since.\textsuperscript{17} The applicability of the solution was broadened considerably by Yang and
Lee's paper, which made clear the connection between a ferromagnetic system and a so-called lattice gas.\(^5\) Nonetheless attention has continued to center on the ferromagnetic applications of the Ising model, while its applicability to fluid systems has been largely neglected. Indeed, Huang expresses a common opinion when he states that a lattice gas does not correspond to any real system in nature.\(^1\) The statement is true if the term lattice gas is taken literally; i.e. if one thinks of the particles as fixed at lattice sites. This is not the point of view adopted in this study. The cellular lattice of the model investigated here serves merely to fix the instantaneous position of the particles in the system and to average the interaction potential over the cell. It will be seen in what follows that this approach leads to a versatile and realistic picture of the behavior of simple fluids.
CHAPTER II

MATHEMATICAL FORMULATION OF THE PROBLEM

A. Fluid System

Consider a system of one-dimensional particles distributed on a line of length L. For convenience, assume periodic boundary conditions, i.e. assume that the line is bent to form a ring so that if we measure distance along the line from some arbitrary origin these distance measurements are modulo L. The boundary conditions are introduced only for mathematical convenience and will clearly not affect the thermodynamics of the system as \( L \to \infty \), i.e. in the thermodynamic limit.

Let the line of length L be divided into N cells so that each cell is of dimension

\[
\ell = \frac{L}{N}
\]  

(1)

The cell parameter, \( \ell \), could be chosen any convenient length. However, it will turn out in the sequel that the most appropriate model is one in which the cell size is chosen equal to the particle size, that is to say the diameter of the particle's effective exclusion sphere. Any other choice of cell size will prove to be a trivial variation of the one adopted here. To fix ideas, we note that \( \ell \) is of the order of \( 10^{-8} \) cm for a typical simple liquid.\(^8,18\)

The potential to be used throughout most of this study is one with a hard-rod repulsive core and long-range attractive tail. A typical potential of this type, and the one assumed hereafter unless otherwise stated, is a modified Lennard-Jones potential:\(^2,3,8\)

\[
V(X) = \begin{cases} 
+\infty, & (X<\ell/2) \\
-\alpha/X^\gamma, & (X>\ell/2)
\end{cases}
\]  

(2)
where $\zeta$ is a parameter fixing the potential depth, while $\gamma$ is a parameter specifying the range of the attractive potential. For the true Lennard-Jones potential $\gamma=6$; however, other ranges are also investigated in this study with results that will be seen to hold considerable interest. Figure 1 gives a comparison of the true Lennard-Jones potential and the modified one assumed for the purpose of this study.

![Comparison of True and Modified Lennard-Jones Potential](image)

**Figure 1. Comparison of True and Modified Lennard-Jones Potential.**

While convenient, adoption of the Lennard-Jones potential is not essential to this study or its conclusions. What is required is a potential with hard core and a long attractive tail. An exponential potential, for instance, of the following form would do equally as well:
\[ V(X) = \begin{cases} +\infty & ; (X \leq \ell/2) \\ -\zeta \exp\{-\gamma(X-\ell)\} & ; (X > \ell/2) \end{cases} \] (3)

For purposes of determining the interaction potential of the system we shall assume that the potential throughout a given cell is uniform and that the interaction potential of two particles is that which would obtain if the particles were perfectly symmetric with their center of mass coinciding with the geometric center of the cell. The following figure illustrates the true versus idealized interaction of two particles.

\[ V(X_1-X_2) = -J|x_1-x_2|^{-\gamma} \]
True Interaction

\[ V = -J(2)^{-\gamma} \]
Idealized Interaction

Figure 2. True and Idealized Interaction Between Two Particles.

The idealized interaction is, of course, a function only of the separation distance between two particles. We may then write the potential as follows:

\[ V_s = -\zeta/S^\gamma_1(1 \leq s < N-1, \text{ mod. } N) \] (4)

where

\[ s = |[X_1]-[X_2]| \]
and \([X_1]\) means "nearest integer equal to or less than \(X_1\)". Distances are measured from an arbitrary origin coinciding with a cell boundary. It will be noted that the potential is defined modulo \(N\) because of the periodic boundary conditions. Thus we have:

\[ V_{N+s} = V_s \]  

(5)

One observes a lack of symmetry in the potential, as illustrated in Figure 3.

![Figure 3. Interaction Potentials of the Typical Ring.](image)

The potential defined in equation (4) seems to depend on how one measures distance around the ring. In truth, this lack of symmetry is trivial, for the interaction around the "long" side of the ring vanishes as \(N \to \infty\). However, to preserve symmetry for finite systems we define a new potential function in keeping with the symmetry of the system:

\[ \phi_s = \frac{1}{2}(V_s + V_{N-s}) \quad (1 \leq s \leq N-1, \mod N) \]  

(6)

The factor of 1/2 has been included in the definition for convenience. We have then

\[ \phi_s = \phi_{N+s} = \phi_{N-s} \quad (1 \leq s \leq N-1, \mod N) \]  

(7)
We have thus far ignored the repulsive part of the potential. Since it has been assumed that the cell parameter, \( l \), is equal to the diameter of the particle's exclusion sphere (i.e., \( l \) is twice the range of the hard-core repulsive potential), and since it was also assumed that a particle is either in one cell or the other (it does not straddle a cell wall), it follows that the repulsive potential is equivalent to an exclusion principle. A cell is either occupied by one particle or it is empty. There can be no partial occupancy, nor can a cell be occupied by more than one particle. It is one of the essential features of the model that some cells may be occupied in the system while, in general, others are empty. One may then label the state of a cell by its occupation number, \( n \), thus:

\[
  n_k = \begin{cases} 
    0 & \text{if the kth cell is empty} \\
    1 & \text{if the kth cell is occupied}
  \end{cases}
\]  

Having built the repulsive potential into the model, so to speak, we are free to define an arbitrary potential for \( V_0 \). It proves most convenient to choose

\[
  V_0 = V_N = 0 \quad \text{(mod. } N) \tag{9}
\]

and therefore:

\[
  \phi_0 = \phi_N = 0 \quad \text{(mod. } N) \tag{10}
\]

So that all summations over potentials, which occur fairly frequently in the theory, may also be carried over the zero cell. There will be occasions in the study, however, when we wish to look explicitly at the effects of the repulsive potential. It will then be necessary to rescind this definition. Such occasions will be pointed out explicitly.

It is now possible to write down the total configurational energy of the system providing we suppose that the total interaction energy of the
system can be obtained by summing all pair interactions. Let \( U_c \) be the configurational energy of the system; then:

\[
U_c = \sum_{r=1}^{N} \sum_{s=1}^{N} r_t n_r n_s \phi_{rs}
\]  

(11)

where the interactions in both directions around the ring have been included. While logically necessary, the contribution around the "long" side of the ring becomes trivial in the thermodynamic limit of interest here. Even for finite systems for which the true Lennard-Jones potential is used with \( \gamma = 6 \) (cf. equation (2)) this contribution becomes negligible for \( N \) larger than about 3.

Normally it would be necessary to add a term to this expression for the configurational energy in order to take account of the interaction of the system with the boundary, i.e. the wall of the containers, the free surface of a liquid, etc. This is obviated in this case by the periodic boundary condition. There is no interaction of the system except with itself.

The assumption that a particle is entirely in one cell or the other, is of course only a mathematical artifice introduced to facilitate writing the configurational energy and assist in evaluating the partition function. The particles will in truth be in constant motion. The total energy of the system is therefore:

\[
H = T + U_c
\]

(12)

where

\[
T = \frac{1}{2m} \sum_{r=1}^{N} p_r^2
\]

(13)

is the kinetic energy contribution, and \( p_r \) is the momentum of the \( r \)-th
particle. It has been assumed here that there are \( n \) particles in the system instantaneously.

We shall suppose that the fluid under consideration is strictly classical, i.e. such fluids as helium, a degenerate Bose gas, etc. are specifically excluded. Extension of the theory to quantum systems, while formally possible, would introduce complications which are not warranted in view of the small number of systems to which they would apply.

Suppose now, that we replace the occupation numbers \( n_k \) by a cell occupation index \( \sigma_k \), defined as follows:

\[
\sigma_k = 2n_k - 1
\]

It is seen that \( \sigma_k \) can take on the following values:

\[
\sigma_k = \begin{cases} 
+1 & \text{if kth cell is occupied } (n_k = 1) \\
-1 & \text{if kth cell is empty } (n_k = 0)
\end{cases}
\]

The transformation from the \( n_k \)'s to the \( \sigma_k \)'s is thus an isomorphism. The energy of the system in terms of the \( \sigma \)'s is:

\[
H = \frac{1}{2m} \sum_{r=1}^{n} p_r^2 + \frac{1}{4} \sum_{r=1}^{N} \sum_{s=1}^{N} (1+\sigma_r)(1+\sigma_r+s)\phi_s
\]

The configurational part of the energy can then be written as:

\[
U_c = \frac{1}{4} \sum_{r=1}^{N} \sum_{s=1}^{N} (1+\sigma_r)(1+\sigma_r+s)\phi_s
\]

\[
= \left( \frac{N}{4} + \frac{1}{2} \sum_{r=1}^{N} \sigma_r \right)\phi + \frac{1}{4} \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_r+s\phi_s
\]

where

\[
\phi \equiv \sum_{s=1}^{N} \phi_s
\]
Use has been made of the fact here that

\[
\sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_{r+s} \phi_s = \sum_{s=1}^{N} \phi_s \sum_{r=1}^{N} \sigma_{r+s}
\]

\[
= \sum_{s=1}^{N} \phi_s \sum_{r=1}^{N} \sigma_r
\]

i.e.

\[
\sum_{r=1}^{N} \sigma_{r+s} = \sigma_{s+1} + \sigma_{s+2} + \ldots + \sigma_{N-1} + \sigma_s
\]

\[
= \sum_{r=1}^{N} \sigma_r
\]

The total energy of the system is then:

\[
H = \frac{1}{2m} \sum_{r=1}^{N} P_r^2 + \left( \frac{N}{4} + \frac{1}{2} \sum_{r=1}^{N} \sigma_r \right) \phi + \frac{1}{4} \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \phi_s
\]

(16b)

If we suppose that there are \( n \) particles in the system but make no other stipulation as to where these particles are, then \( \binom{N}{n} \) distinct micro-states of the system correspond to this specification, since there are

\[
\frac{N!}{n!(N-n)!} = \binom{N}{n}
\]

ways of distributing \( n \) identical particles among \( N \) cells. Each of the \( \binom{N}{n} \) states is characterized by a particular set of cell configurations, i.e. by a particular set of values of the parameters \( \{\sigma\} \) for the system. Any configuration is acceptable, providing it satisfies the consistency condition:

\[
\sum_{k=1}^{N} n_k = \frac{1}{2} \sum_{k=1}^{N} (1+\sigma_k) = \frac{1}{2} \left( N + \sum_{k=1}^{N} \sigma_k \right) = n
\]
or
\[ \sum_{k=1}^{N} \sigma_k = 2n - N \] (20)

It will be convenient for later purposes to define a slightly different parameter as follows:
\[ L = \frac{1}{N} \sum_{k=1}^{N} \sigma_k = \frac{2n}{N} - 1 = 2r - 1 \] (21)

where
\[ r = \frac{n}{N} \]

We note in passing that
\[ \sum_{k=1}^{N} \sigma_k = N_+ - N_- \] (22)

where
\[ N_+ \] is the total number of cells with \( \sigma = +1 \)
\[ N_- \] is the total number of cells with \( \sigma = -1 \)

If we also make use of the obvious identity:
\[ N = N_+ + N_- \] (23)

then we regain equation (20) from (22).

Using classical Boltzmann statistics, the probability that the system is to be found in the \( i \)th configurational state is
\[ W_i = \frac{\exp{-\beta H(\{\sigma\},i)}}{\sum_{\sigma} \exp{-\beta H(\{\sigma\})}} \] (24)

\[ = \frac{\exp{-\beta U_c(\{\sigma\},i)}}{Z_n} \]

where
\[ Z_n = \sum_{\sigma} \exp{-\beta U_c(\{\sigma\})} \] (25a)

and
\[ \beta = 1/(kT) \]
and where $\sum_{<o>}$ means the sum over all sets of $o$ consistent with condition (20). $Z_n$ is the configurational part of the partition function.

Written out explicitly it is:

$$Z_n = \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp(-\beta U_c(\{\sigma\}))$$

$$= \sum_{\sum_{k=1}^{N} \sigma_k = 2n-N}^{1} \prod_{r=1}^{N} \sigma_r \prod_{s=1}^{N} \sigma_{r+s} \frac{1}{2} \prod_{r=1}^{N} \sigma_r$$

and

$$Z_n = \exp(-\beta N/4\phi) \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp\left(-\frac{1}{4\beta} \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \phi \frac{1}{2} \sum_{r=1}^{N} \sigma_r \right)$$

$$\left[ \sum_{k=1}^{N} \sigma_k = 2n-N \right] \tag{25b}$$

In order to obtain the macrocanonical partition function for a system of $n$ particles it is most convenient to consider first the usual integral formulation:

$$Q_n = \frac{1}{n!h^n} \int dp_1 \cdots \int dp_n \int dx_1 \cdots \int dx_n \exp\left(-\frac{\beta}{2m} \sum_{r=1}^{N} p_r^2 \right)$$

$$\exp\left(-\frac{\beta}{2m} \sum_{r=1}^{N} p_r^2 \right) \exp\left(-\beta U_c(x_1, \cdots x_n) \right)$$

$$= \frac{1}{n!h^n} \left( \frac{2\pi m}{\beta} \right)^{n/2} \int dx_1 \cdots \int dx_n \exp\left(-\beta U_c(x_1, \cdots x_n) \right)$$

$$= \frac{1}{n!\lambda^n} \int dx_1 \cdots \int dx_n \exp\left(-\beta U_c(x_1, \cdots x_n) \right) \tag{26}$$

where $\lambda$ is the thermal wavelength defined as follows:

$$\lambda = (\beta h^2/2\pi m)^{1/2} \tag{27}$$
and where it was assumed that the kinetic and configurational parts of
the energy are uncorrelated.

Consider now the configurational part of the partition function

\[ Z'_n = \int dx_1 \cdots \int dx_n \exp\left\{-\beta U_c(x_1, \cdots, x_n)\right\} \]

If \( U_c = 0 \), then \( Z'_n = V^n \), where \( V \) is the "volume" of the system; i.e. \( V = L \) in the case of the one-dimensional system under consideration. However, for purposes of ease in generalization later, when we shall also con-
sider two- and three-dimensional models, we shall use the symbol \( V \), understanding that in the present instance it is synonymous with \( L \).

Now, we have expressed \( U_c \) as a function of the parameter \( \sigma \). We therefore write the configurational partition function as a discrete sum over all sets of \( \sigma \)'s consistent with the requirement that there be \( n \) particles in the system, as was done in equation (25). In going over from an integral to a discrete summation, however, we must take due ac-
count of the volume of the system:

\[ Z'_n = \int dx_1 \cdots \int dx_n \exp\left\{-\beta U_c(x_1, \cdots, x_n)\right\} \]

\[ = V^n \alpha_n \sum_{\sigma} \exp\{-\beta U_c(\{\sigma\})\} \]

\[ = V^n \alpha_n Z_n \]

Where \( \alpha_n \) is a constant of proportionality to be determined. To evaluate \( \alpha_n \), observe that any one of the configurations of the system is character-
ized by having a particular set of \( n \) cells with \( \sigma = +1 \), while in the remain-
ing \( (N-n) \) cells \( \sigma = -1 \). There are \( \binom{N}{n} \) ways of obtaining such a distribution of \( \sigma \)'s. Hence we find

\[ \alpha_n^{-1} = \binom{N}{n} \]
so that

$$Z'_n = V^n Z_n^\binom{N}{n} \quad (29)$$

with $Z_n$ defined by equation (25). The canonical partition function is therefore (see equation (26)):

$$Q_n = \frac{V^n}{n! \binom{N}{n} \lambda^n} Z_n = \frac{V^n (N-n)!}{N! \lambda^n} Z_n \quad (30a)$$

Consider now the following identity:

$$\sum_{n=0}^{N} \binom{N}{n} x^n = (1+x)^N$$

and suppose that $X=Y/N$, then

$$\sum_{n=0}^{N} \binom{N}{n} x^n = \left(1+\frac{Y}{N}\right)^N = \sum_{n=0}^{N} \binom{N}{n} \left(\frac{Y}{N}\right)^n$$

But

$$\lim_{N \to \infty} \left(1+\frac{Y}{N}\right)^N = e^Y = \sum_{n=0}^{\infty} \frac{1}{n!} Y^n$$

Consequently,

$$\lim_{N \to \infty} \left\{ \frac{N}{n!} \binom{N}{n} \frac{1}{n!} Y^n \right\} = 0$$

The identity must of course hold for any value of the variable $Y$. We conclude then that for large $N$, the following relation holds:

$$\lim_{N \to \infty} n! \binom{N}{n} = \lim_{N \to \infty} N^n \quad (31)$$

Consequently, if the size of the system is not too small we may write:

$$Q_n = \left(\frac{V}{\lambda N}\right)^n Z_n = \left(\frac{s}{\lambda}\right)^n Z_n \quad (30b)$$
since
\[ \frac{V}{N} = \frac{L}{N} = \ell \]

where \( \ell \) is the cell parameter previously defined.

For the purpose of the present problem it is preferable to use a grand partition function for two reasons: first, we shall be concerned with systems subject to phase transitions so that the number of particles in the system under consideration cannot be thought of as fixed. Secondly, the restriction occurring in the sum of \( \sigma \)'s (see for example equation (25b)) is awkward mathematically. Transition to a grand-canonical ensemble will eliminate this restriction.

Let \( g \) be the Gibbs potential per particle, and let
\[ \xi = e^{\beta g} \]  
(32)

The grand-canonical partition function may then be written as follows:
\[
Q_N = \sum_{n=0}^{N} \left( \frac{\xi}{\lambda} \right)^n \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp\{-\beta U_c(\{\sigma\})\} \left( \sum_{k=1}^{N} \sigma_k = 2n-N \right)
\]
(33)

For convenience let
\[ e^{\beta \mu} = \left( \frac{\xi}{\lambda} \right) \]
(34)

Recalling that
\[ n = \sum_{k=1}^{N} n_k = \frac{1}{2} \sum_{k=1}^{N} (1+\sigma_k) = \frac{N+1}{2} \sum_{k=1}^{N} \sigma_k \]

equation (33) may be
rewritten as follows:

\[ Q_N = \exp\left(\frac{1}{2} \beta N(\mu - \frac{1}{2} \phi)\right) \sum_{n=0}^{N} \prod_{1 \leq r \leq \frac{1}{2}} \prod_{1 \leq s \leq \frac{1}{2}} \exp\left(-\frac{1}{4} \beta \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_r + \frac{1}{2} \phi \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \cdot \sigma_r + \frac{1}{4} \beta (\mu - \phi) \sum_{r=1}^{N} \sigma_r \right) \]

\[ \left(\sum_{k=1}^{N} \sigma_k = 2n-N \right) \]

(35a)

It was observed before that for a given \( n \) there are \( \binom{N}{n} \) terms in the sums of \( \sigma \)'s, i.e. there are \( \binom{N}{n} \) sets of particular \( \sigma \)'s that satisfy the stated restriction. If it were not for this restriction, the sums of \( \sigma \)'s would, of course, have \( 2^N \) terms since there are \( N \) \( \sigma \)'s and each can take on two possible values. As we now sum over all possible \( n \), we pick up the entire set of \( 2^N \) terms, i.e.

\[ \sum_{n=0}^{N} \sigma_1 = -1 \sum_{n=0}^{N} \sigma_N = -1 \sum_{1 \leq r \leq \frac{1}{2}} \sum_{1 \leq s \leq \frac{1}{2}} F(\{\sigma\}) = \sum_{\sigma_1 = -1}^{1} \sum_{\sigma_N = -1}^{1} F(\{\sigma\}) \]

\[ \left(\sum_{k=1}^{N} \sigma_k = 2n-N \right) \]

Thus we find that

\[ \sum_{n=0}^{N} \sum_{\sigma_1 = -1}^{1} \sum_{\sigma_N = -1}^{1} \sum_{1 \leq r \leq \frac{1}{2}} \sum_{1 \leq s \leq \frac{1}{2}} F(\{\sigma\}) = \sum_{\sigma_1 = -1}^{1} \sum_{\sigma_N = -1}^{1} F(\{\sigma\}) \]

where the sum on the right hand side is unrestricted.

The grand canonical partition function can therefore be written as:

\[ Q_N = \exp\left(\frac{1}{2} \beta (\mu - \frac{1}{2} \phi) N\right) \sum_{\sigma_1 = -1}^{1} \sum_{\sigma_N = -1}^{1} \exp\left(-\frac{1}{4} \beta \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_r + \frac{1}{2} \phi \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \cdot \sigma_r + \frac{1}{4} \beta (\mu - \phi) \sum_{r=1}^{N} \sigma_r \right) \]

(35b)
It is convenient, now, to make the following definitions:

\[ \vartheta_s = \frac{1}{4} \beta \phi_s ; \quad \Theta = \sum_{s=1}^{N} \theta_s = \frac{1}{4} \beta \phi \]  

\[ \nu = \frac{1}{2} \beta (\mu - \phi) \]  

In terms of these parameters the partition function is:

\[ \mathcal{Q}_N = \exp\{N(\nu - \Theta)\} \sum_{\sigma_1 = -1}^{1} \cdots \sum_{\sigma_N = -1}^{1} \exp\left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \theta_s + \nu \sum_{r=1}^{N} \sigma_r \right\} \]

\[ = C_N \Xi_N \]

where

\[ C_N = \exp\{N(\nu - \Theta)\} \]

\[ \Xi_N = \sum_{\sigma_1 = -1}^{1} \cdots \sum_{\sigma_N = -1}^{1} \exp\left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \theta_s + \nu \sum_{r=1}^{N} \sigma_r \right\} \]

This is the form in which the partition function will generally be used in what follows. It should be observed that each term in this sum of \(2^N\) terms represents one possible configuration of the system. One can think of each term as being a "snapshot" of the system at a particular instant of time. If one waits sufficiently long, one will obtain such "snapshots" of all possible states. However, the probability of a given configuration is not the same as that of all other configurations. Indeed, the probability of a configuration is:

\[ W_i = \Xi_N^{-1} \exp\left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r i \sigma_{r+s} \theta_s + \nu \sum_{r=1}^{N} \sigma_r \right\} \]
where $\sigma_r^i$ indicates the occupancy parameter of the $r$th cell corresponding to the $i$th configuration. Each of these configurations represents a microstate of the system. What we observe macroscopically, however, are macrostates, i.e. for example a state corresponding to a particular $n$. The probability of observing such a state is:

$$W(n) = \sum'_i w_i$$

(39)

where the symbol $\sum'_i$ means summation over all microstates that are consistent with the stated conditions of the given macrostate. The sum in (37), thus, represents a sum over all possible system configurations.

The assumptions on which the partition function in equation (35) is based are summarized once more below:

1. The system has periodic boundary conditions.
2. The system is comprised of $N$ cells, each of length $\ell$.
3. The cell parameter $\ell$ is equal to the diameter of the exclusion sphere of a particle.
4. A particle lies entirely in the cell in which its center of mass is instantaneously located.
5. There is no correlation between the particle momenta and their interaction potentials.
6. The sum of all pair interactions will yield the total configurational energy of the system.
B. Ferromagnet:

While this study is concerned primarily with a fluid system, it will be desirable occasionally to extend results to the case of a ferromagnet or to compare results with known ferromagnetic ones. The appropriate ferromagnetic partition function will therefore be developed in this section.

The situation differs somewhat here from the fluid case just considered. Suppose now that the system consists of N lattice sites spaced on a ring and each site occupied by a particle with spin $\sigma$. Only two possible spin states are possible: $\sigma=+1$ and $\sigma=-1$.

Suppose that the exchange energy between two particles at lattice sites separated by k lattice parameters is $J_k$. Again, let us introduce a potential that is suitable to the symmetry of the lattice as follows:

$$\phi_k = \frac{1}{2}(J_k + J_{N-k})$$  \hspace{1cm} (40)

so that:

$$\phi_k = \phi_{k+N} = \phi_{k-N}$$  \hspace{1cm} (41)

We shall also require, as in the case of the fluid, that

$$\phi_0 = \phi_N = 0$$  \hspace{1cm} (42)

so as to exclude spurious self-energy terms.

Let the magnetic moment of the particles be $m$, and suppose that $B$ is an external magnetic field in the same direction as the positive spin. In the ferromagnetic case we shall neglect all kinetic contributions to the energy by supposing that all particles are firmly fixed at their lattice positions. In addition, we shall neglect all energy contributions other than the spin interactions.
With these assumptions, the energy of the system is:

\[
H = \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \phi_s - mB \sum_{r=1}^{N} \sigma_r
\] (43)

The partition function of the system is then:

\[
Q_N = \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp\{-\beta H(\{\sigma\})\}
= \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp\{-\beta \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \phi_s + \beta mB \sum_{r=1}^{N} \sigma_r\}
\] (44a)

Now let

\[
\theta_s = -\beta \phi_s
\] (45a)

\[
\nu = \beta mB
\] (45b)

The partition function can then be written as follows:

\[
Q_N = \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp\{\sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \theta_s + \nu \sum_{r=1}^{N} \sigma_r\} = \Xi_N
\] (44b)

This is the form of the ferromagnetic partition function that will be used in this study. There are obvious similarities between the partition functions of the fluid and ferromagnetic systems. These will be explored in the next section.
C. Comparison of the Fluid and Ferromagnetic Systems:

In comparing the partition function of the fluid with that of the ferromagnet care is necessary in remembering that the former is the partition function of a grand canonical ensemble, while in the latter the number of particles is fixed.

Keeping this in mind one finds that

\[ Q_N = \exp\{N(v-\theta)\} \prod_{\sigma_1=-1}^{1} \prod_{\sigma_N=-1}^{1} \exp\left( \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_r + s + \nu \sum_{r=1}^{N} \sigma_r \right) \]

\[ = \exp\{N(v-\theta)\} q_N = \exp(\beta pV) \]  

(35c)

where

\[ q_N = \prod_{\sigma_1=-1}^{1} \prod_{\sigma_N=-1}^{1} \exp\left( \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_r + s + \nu \sum_{r=1}^{N} \sigma_r \right) \]

(44b)

\[ = \exp(-\beta F) \]

and \( q_N \) is the partition function of the fluid system, \( p \) is the pressure of the system, \( V \) its total "volume" (i.e. \( V=L \) in the case of our linear model), \( q_N \) is the ferromagnetic partition function, and \( F \) is the Helmholtz free energy of the system. Here the well-known relations:

\[ q_N = \exp(\beta pV) \]  

(46a)

and

\[ q_N = \exp(-\beta F) \]  

(46b)

were used.

We are therefore led to the following correspondences (see equations (34), (35), (36), (40), (44), and (45)):
Parameter & Fluid & Ferromagnet \\
\( v \) & \( \frac{1}{2} \beta (u-\phi) \) & \( \beta mB \) \\
 & \( = \frac{1}{2} \left[ \ln \left( \frac{2\xi}{\lambda} \right) - \beta \phi \right] \) & \\
\( \theta_r \) & \( -\frac{1}{4} \phi_r \) & \( -\beta \phi_r \) \\
 & \( = -\frac{1}{8} \beta (V_r + V_{N-r}) \) & \( = -\frac{1}{2} \beta (J_r + J_{N-r}) \) \\
\( V_r \) & & \( 4J_r \)

In addition we have from equation (35c) and (44b) above:

\[
\beta pV = N(v-\theta) - BF
\]  
(47a)

where the left-hand side applies to the fluid system and the right-hand side to the ferromagnet. Or:

\[
pV = N \left[ mB + \frac{1}{2} \sum_{s=1}^{N} (J_s + J_{N-s}) \right] - F
\]  
(47b)

Another relation that will be useful later can be derived by considering the sum \( \sum_{r=1}^{N} \sigma_r \). In the case of the fluid system it has already been noted that:

\[
\sum_{r=1}^{N} \sigma_r = N_+ - N_- = 2n - N
\]  
(48)

where \( n \) is the number of particles in the system corresponding to that particular configuration. Therefore

\[
\frac{1}{N} \sum_{r=1}^{N} \sigma_r = 2 \frac{\langle n \rangle}{N} - 1 = 2\rho - 1
\]  
(49)
where:

\[ \rho \equiv \frac{<n>}{N} \]  

(50)

Here \( <A> \) denotes an ensemble average of the parameter (or operator) \( A \) defined as follows:

\[ <A> = \frac{\sum_{\sigma_1} \cdots \sum_{\sigma_N} A \exp{-\beta H}}{\sum_{\sigma_1} \cdots \sum_{\sigma_N} \exp{-\beta H}} \]  

(51)

Thus, \( <n> \) represents the average number of particles in the system, while \( \rho \) may be thought of either as a dimensionless density which is related to the normal density \( \tilde{\rho} \) as follows:

\[ \tilde{\rho} = \frac{<n>}{V} = \frac{<n>}{L} = \frac{<n>}{N\xi} = \rho/\xi \]  

(52)

Alternatively it is possible to adopt a system of units such that \( \xi=1 \). In this case \( \rho \) is dimensionally the true density of the system. Both points of view are useful at times.

In the case of the ferromagnet we have

\[ \frac{1}{N} \sum_{\tau=1}^{N} \sigma_{\tau} = \frac{1}{N} <N_{+} - N_{-}> = M/m \]

where \( M \) is the magnetization per spin. The total magnetization of the system is:

\[ M = NM = m <(N_{+} - N_{-})> = m \sum_{\tau=1}^{N} \sigma_{\tau} \]

We have the following relation then:

\[ 2\rho - 1 = \frac{M}{m} \]

or

\[ \rho = \frac{1}{2}(1 + \frac{M}{m}) \]  

(53)
One notes furthermore that

\[
\langle \sum_{r=1}^{N} \sigma_r \rangle = \left\{ \prod_{r=1}^{N} \left( \sum_{\sigma_r} \exp \left\{ \sum_{s=1}^{N} \sigma_r \sigma_s + \beta \sum_{s=1}^{N} \sigma_s \right\} \right) \right\}^{-1} \left\{ \prod_{r=1}^{N} \sum_{\sigma_r} \exp \left\{ \sum_{s=1}^{N} \sigma_r \sigma_s + \beta \sum_{s=1}^{N} \sigma_s \right\} \right\}
\]

\[
= \frac{\partial}{\partial \beta} \left( \ln Q_N \right) \beta
\]

And using equation (35c) we have:

\[
\langle \sum_{r=1}^{N} \sigma_r \rangle = \frac{\partial}{\partial \beta} \left\{ \ln Q_N \right\} \beta - N
\]

so that

\[
2\rho - 1 = \frac{1}{N} \langle \sum_{r=1}^{N} \sigma_r \rangle = \frac{1}{N} \frac{\partial}{\partial \beta} \ln Q_N - 1
\]

\[
\rho = \frac{1}{2} \frac{\partial}{\partial \beta} \left( \ln Q_N \right) \beta
\]

This result will be useful later.

A summary of the results of this section can be presented in the following tabular form:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fluid System</th>
<th>Magnetic System</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu )</td>
<td>( \frac{1}{2} \ln \left( \frac{\beta \xi}{\lambda} \right) - \beta \phi )</td>
<td>( \beta mB )</td>
</tr>
<tr>
<td>( \theta )</td>
<td>( -\frac{1}{4} \beta \phi )</td>
<td>( -\beta \phi )</td>
</tr>
<tr>
<td>( r )</td>
<td>( V_r )</td>
<td>( 4J_r )</td>
</tr>
</tbody>
</table>
(TABLE I - Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fluid System</th>
<th>Magnetic System</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pV$</td>
<td></td>
<td>$N\left(mB + \frac{1}{2} \sum_{r=1}^{N} (J_r + J_{N-r})\right) - F$</td>
</tr>
<tr>
<td>$\rho$</td>
<td></td>
<td>$\frac{1}{2}(1+\lambda/m)$</td>
</tr>
</tbody>
</table>
D. Extension to More General Systems:

(1) Multidimensional Systems:

The one-dimensional system considered above in which each particle interacts with every other one is readily extended to systems embedded in spaces of higher dimensionality but with more limited interactions. Indeed, it will emerge in what follows that the two and three dimensional Ising models as they are usually considered are but particular applications of this more general one-dimensional system providing one adopts suitable boundary conditions.

To this end, consider first a two-dimensional square array in which the particles interact only with their nearest neighbors, i.e. with particles in adjacent cells. There is no interaction between particles separated by greater distances. If we continue to use the same interaction potential as before, the nearest-neighbor interaction is given by

\[ V_1 = -\zeta \]  

in the case of a fluid system and by

\[ J_1 = -J \]  

in the case of a ferromagnet. Here \( \zeta \) and \( J \) are both positive constants.

Consider now the linear chain wrapped around a torus as shown in Figure 4:

![Figure 4. Toroidal Topology of 2-Dimensional Model.](image-url)
Only part of the chain is shown to avoid confusion. The chain in fact continues completely around the torus until its end merges again into its beginning, i.e. cell N is once more adjacent to cell 1 so that the periodic boundary conditions of the one-dimensional model are preserved. However, we now change our point of view slightly from the one-dimensional case. Here cells that are contiguous to one another in parallel segments of the chain are also considered nearest neighbors. Typical of such pairs in the example of Figure 4 are 1 and 7, 2 and 8, 3 and 9, 7 and 13, etc. in addition to the usual pairs along the chain. If the system under consideration is a fluid, then the numbered dots in Figure 4 represent cell centers; these cells may or may not be occupied. On the other hand, if the system is a ferromagnet then the dots are particles with spins.

The wrapping of the string around a torus is, of course, only an artifice in order to obtain the correct boundary conditions. The two-dimensional nature of the array will be more apparent if we now unfold the array from the torus, as shown in Figure 5:

Figure 5. 2-Dimensional Model in Plane Projection.
Figure 5 must be thought of as a plane projection of an array like the one in Figure 4 (note that the systems in the two figures are not identical. Figure 5 shows a system of 16 cells, whereas Figure 4 exhibits a larger system). The dotted lines in Figure 5 represent boundary conditions introduced by the toroidal topology that are tantamount to nearest-neighbor interactions.

In order to express these conditions in mathematical terms, suppose now that the system consists of $N$ cells with $m$ cells per row ($m=4$ in Figure 5) and $n$ rows in the array ($n=4$ in Figure 5), so that

$$N = nm$$

(59)

We must remember that terms like "row" are merely picturesque expressions referring to plane projections like Figure 5. In truth we have only the chain wrapped about the torus as in Figure 4. However, as $N \rightarrow \infty$, $n \rightarrow \infty$, and $m \rightarrow \infty$ the distinction just made becomes academic. To creatures living on the surface of the torus, the array is indeed a two-dimensional one as depicted in the last figure. We now take account of the boundary conditions as follows:

$$V_r = \begin{cases} 
-\xi, & r = 1, \text{ m (mod. N)} \\
0, & r \neq 1, \text{ m (mod. N)} 
\end{cases}$$

(60a)

$$\phi_r = \frac{1}{2}(V_r + V_{N-r})$$

$$J_r = \begin{cases} 
-J, & r = 1, \text{ m (mod. N)} \\
0, & r \neq 1, \text{ m (mod. N)} 
\end{cases}$$

(60b)

$$\phi_r = \frac{1}{2}(J_r + J_{N-r})$$
With the use of the potential (60a) in the partition function (35) or of the exchange energy (60b) in the partition function (44) the respective partition functions become those of a two-dimensional system. In the two-dimensional case, just as in the one-dimensional one, the cells provide merely a convenient space grid for locating the particles of the system. They must not be thought of as a crystal-type lattice imparting a symmetric structure to the system that does not actually exist.

A three-dimensional system can be structured from the one-dimensional one in equally as straightforward a fashion. However, in the three-dimensional case we must think of the linear chain wound on a four-dimensional "torus" in order to yield the correct boundary conditions. It is, of course, not possible to picture this arrangement and we must be content with stating the boundary conditions mathematically. To do so, consider the projection of a typical three-dimensional array shown in Figure 6:

![Figure 6. 3-Dimensional Array](image)
The figure represents a three-dimensional system consisting of 64 cells whose centers are denoted by dots. Some of the possible nearest-neighbor bonds are shown; others have been omitted to avoid confusion. It must be remembered that these bonds are active only when both cells connected by a given bond are occupied.

If we suppose that the general system consists of \( m \) cells per row, \( n \) rows per layer, \( p \) layers so that

\[
N = mnp
\]

then, letting \( k = mn \), the boundary conditions to be satisfied are:

- cell 1 contiguous to cell \( N \) (64 in Fig. 6)
- cell \( r \) contiguous to cell \( r+m \) (\( r+4 \) in Fig. 6)
- cell \( r \) contiguous to cell \( r+k \) (\( r+16 \) in Fig. 6)
- cell \( r \) contiguous to cell \( r+1 \)

All of these conditions are, of course, modulo \( N \). In terms of the appropriate potentials these conditions become:

\[
V_r = \begin{cases} 
-\varsigma, & r = 1, m, k \pmod{N} \\
0, & r \neq 1, m, k \pmod{N}
\end{cases} \tag{62a}
\]

\[
\phi_r = 1/2(V_r + V_{N-r})
\]

\[
J_r = \begin{cases} 
-J, & r = 1, m, k \pmod{N} \\
0, & r \neq 1, m, k \pmod{N}
\end{cases} \tag{62b}
\]

\[
\phi_r = 1/2(J_r + J_{N-r})
\]
Substitution of these potentials in the appropriate partition functions will then yield the correct three-dimensional partition function for nearest-neighbor interactions.

Only the simplest two and three dimensional models have been considered above. More complicated interactions can be accommodated also within the framework sketched above. To do so we need only include additional interactions of appropriate strength. To illustrate this, consider the two-dimensional model once more. Suppose one wishes to treat an anisotropic system in which the horizontal interactions are not the same as the vertical ones. This requires only the following change in the potential:

\[
V_r = \begin{cases} 
-\zeta_1, & r = 1 \pmod{N} \\
-\zeta_2, & r = m \pmod{N} \\
0, & r \neq 1, m
\end{cases} \quad (63)
\]

\[
\phi_r = \frac{1}{2}(V_r + V_{N-r})
\]

If we wish to include next-nearest-neighbor interactions also, as another example, then the potential can be written as follows in the two-dimensional case:

\[
V_r = \begin{cases} 
-\zeta_1, & r = 1 \\
-\zeta_2, & r = m-1, m+1 \\
-\zeta_3, & r = m \\
0, & r \neq 1, m-1, m, m+1
\end{cases} \pmod{N} \quad (64)
\]

Figure 7 shows this interaction for one set of four contiguous cells.
Clearly, similar changes can be introduced in the three-dimensional model if it is desired to consider additional or anisotropic interactions.

These modifications are, however, of little interest in the model of a simple fluid considered here. This is because we use the cell structure only as a space grid, as stated before. The particles are not tied to lattice sites, hence all sites are equivalent and little meaning can seemingly be attached to anisotropic interactions.

It will have been observed that the method of converting the basic one-dimensional system into two- or three-dimensional systems with more limited interactions introduces spurious interactions on the boundaries of the system. In Figure 6, for instance, such interactions would occur between particles 4 and 5, 8 and 9, 13 and 17, 14 and 18, 61 and 13, 62 and 14, to name just a few. While these have a noticeable effect in small systems, as we shall see in Chapter VIII, their effect becomes negligible in the thermodynamic limit, for then $N$, $m$, and $k$ all go simultaneously to infinity.

(2) **Multiple Cell Occupancy:**

Within the formalism of the Ising model cell occupancies other than 0 and 1 can readily be accommodated, providing intermediate occupancies are not considered. Thus, let a given cell either be empty or be occupied by $m$ particles. Then the configurational energy of the
The system is:

\[ U_c = \frac{m^2}{4} \sum_{r=1}^{N-1} (1+\sigma_r) (1+\sigma_{r+s}) \phi_s + \frac{1}{4} m^2 (m-1) \phi_0 \sum_{r=1}^{N} \sigma_r \]

\[ = \frac{N}{4} [m^2 \phi' + m(m-1) \phi_0] + \frac{1}{2} [m^2 \phi' + m(m-1) \phi_0] \sum_{r=1}^{N} \sigma_r + \frac{m^2}{2} \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \phi_s \]

where

\[ \phi' = \sum_{r=1}^{N-1} \phi_r; \quad \phi_0 = \text{average interaction potential of particles in the same cell.} \]

The activity of the system is:

\[ \exp(n \beta \mu) = (e^{\xi/\lambda})^n = \exp\left(\frac{m^2}{2} \mu \sum_{r=1}^{N} (1+\sigma_r)\right) = \exp\left(\frac{1}{2} \beta m \mu \sum_{r=1}^{N} \sigma_r\right) \]

The partition function of the system is then:

\[ Q_N = \exp\left(\frac{1}{2} \beta m \mu (1+1/2(1+m)) \phi_0 - \frac{1}{2} m^2 \phi_0 \right) \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp\left(-\frac{1}{4} \beta m^2 \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} \phi_s \right) \]

\[ \cdot \exp\left(\frac{1}{2} \beta m (1+1/2(1+m)) \phi_0 - \frac{1}{2} m^2 \phi_0 \right) \sum_{r=1}^{N} \sigma_r \]

If we now make the following definitions:

\[ \theta_s = -\frac{1}{4} \beta m^2 \phi_s \]

\[ \nu = \frac{1}{2} \beta m (1+1/2(1+m)) \phi_0 - \frac{1}{2} m^2 \phi_0 \]

\[ \theta = \sum_{r=1}^{N} \theta_r = -\frac{1}{4} \beta m^2 \phi \]

\[ \theta' = \sum_{r=1}^{N-1} \theta_r = -\frac{1}{4} \beta m^2 \phi' \]
Then:

$$Q_N = \exp\{N(\nu - \Theta')\} \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp\left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma_r \sigma_{r+s} + \nu \sum_{r=1}^{N} \sigma_r \right\}$$

The partition function therefore has the same formal appearance as the partition function for the case $m=1$ (cf. equation (35)) if we remember that in that case $\phi_0=0$ so that $\phi=\phi'$, $\Theta=\Theta'$.

If we allow multiple occupancy, we must, of course, also increase the cell size appropriately. Thus, in the case of cell occupancy by $m$ particles, a new cell parameter $\lambda$ needs to be defined:

$$\lambda = m\lambda$$

This entails a serious disadvantage insofar as the present model is concerned, for we reduce the fineness of our space mesh by this stratagem. Another very considerable difficulty ensues as well: while one can insure that the hard-core repulsive potential is obeyed on the average by the above choice of $\lambda$, we cannot be sure that the $m$ particles inside a given cell do not violate this potential. In short, we create in this way a type of "nuclear well" as it were which presents a hard core barrier to particles on the outside but not to particles inside the well. While this may be of advantage under certain conditions, it is not an acceptable model for the fluid and the potential which we have assumed above.

The matter of multiple cell occupancy will therefore not be pursued further in the present context.
CHAPTER III

MATRIX FORMULATION OF THE PROBLEM

The motivation for attempting a matrix solution of the problem is, of course, the success which Onsager achieved in solving the two-dimensional Ising problem (with nearest-neighbor interactions) by this method. Actually, the original matrix formulation is due to Kramers and Wannier who showed that many of the properties of the two-dimensional ferromagnet can be obtained from such a formulation even if the solution of the problem is not known. Onsager's solution was later reformulated by Bruria Kaufman on the basis of a spinor formalism that has its origin in a 2N-dimensional representation of the quaternion algebra developed by Brauer and Weyl a decade earlier. The matrix formulation of the present problem follows approximately the latter method, although important differences are introduced by the full range of interactions considered here and the difference in boundary conditions.

Let us consider the partition function in the form:

\[ Q = A \sum_{\{\sigma\}} \exp\left\{ \sum_{r=1}^{N} \left( \sum_{s=1}^{N} \sigma_r \sigma_{r+s} + \theta \sum_{r=1}^{N} \sigma_r \right) \right\} \]  

where

\[ \sum_{\{\sigma\}} \equiv \sum_{\sigma_1=-1}^{1} \sum_{\sigma_N=-1}^{1} \]

\[ A = \begin{cases} \exp\{N(\nu-0)\} & \text{(fluid system)} \\ 1 & \text{(ferromagnet)} \end{cases} \]

\[ Q = \begin{cases} Q_N & \text{(fluid system)} \\ Q_N & \text{(ferromagnet)} \end{cases} \]
and the parameters $\theta_r$ and $\omega$ are as previously defined (see the Table I above).

Let $\mu_i$ be a state vector representing the state of the ith cell or of the ith particle in the case of the ferromagnet. In order to avoid unnecessary repetition in what follows, the language appropriate to the fluid system will be used where no ambiguity results therefrom. Also, let $Z$ be an operator defined as follows:

$$Z\mu_i = \sigma_i \mu_i$$

where $\mu_i = 1$ or $-1$ as previously defined. Hence the eigenvalues of $Z$ are 1 and $-1$. A possible, though of course not unique representation of $\mu_i$ is as follows:

$$\mu_i = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$a = \begin{cases} 1 & \text{if the ith cell is occupied} \\ 0 & \text{if the ith cell is empty} \end{cases}$$

$$b = \begin{cases} 0 & \text{if the ith cell is occupied} \\ 1 & \text{if the ith cell is empty} \end{cases}$$

The two possible states are then:

$$\mu_i^+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \mu_i^- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Clearly $\mu_i$ is a two-dimensional spinor. The operator $Z$ can be represented in the same space in which the $\mu_i$'s are the state vectors as follows:

$$Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
One confirms readily that in this representation
\[ Z\mu_i^+ = \mu_i^+ \]
\[ Z\mu_i^- = -\mu_i^- \]

Other operators that will be needed in the sequel are \( x \) and \( y \) defined as follows:
\[ x\mu_i^+ = \mu_i^-; \quad x\mu_i^- = \mu_i^+ \quad (74a) \]
\[ y\mu_i^+ = i\mu_i^-; \quad y\mu_i^- = -i\mu_i^+ \quad (74b) \]

Representations of these two operators in the same space are
\[ x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (75a) \]
\[ y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (75b) \]

These operators, in the two-dimensional representation above, are of course the well-known Pauli spin matrices. More important in what follows is that these operators form part of a quaternion algebra. Their abstract properties, which we shall need below, are:
\[ [x,y]_+ = [x,z]_+ = [y,z]_+ = 0 \quad (76a) \]
\[ [x,y]_- = 2iz; \quad [y,z]_- = 2ix; \quad [z,x]_- = 2iy \quad (76b) \]
where
\[ [A,B]_+ = AB + BA \]
\[ [A,B]_- = AB - BA \]
\[ x^2 = y^2 = z^2 = I \quad (76c) \]
where \( I \) is the identity in the appropriate representation.
Let us next define a new state vector as follows:

$$\psi_\alpha = |\mu_1^\alpha, \mu_2^\alpha, \mu_3^\alpha, \ldots, \mu_N^\alpha>$$

(77a)

where $\mu_i^\alpha$ is the state vector previously defined, with the superscript denoting the $\alpha$th state of the $i$th cell, i.e. $\mu_i^\alpha = \mu_i^+$ or $\mu_i^-$ depending on the state of the $i$th cell. A convenient representation of $\psi$ is a $2^N$ dimensional one as follows:

$$\psi_\alpha = \mu_1^\alpha \otimes \mu_2^\alpha \otimes \cdots \otimes \mu_N^\alpha$$

(77b)

The symbol $\otimes$ is used to denote a matrix direct product defined as follows:

$$A = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{bmatrix}, \quad B = \begin{bmatrix} b_{11} & b_{12} & \cdots & b_{1n} \\ b_{21} & b_{22} & \cdots & b_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ b_{n1} & b_{n2} & \cdots & b_{nn} \end{bmatrix}$$

then

$$A \otimes B = \begin{bmatrix} a_{11}B & a_{12}B & \cdots & a_{1n}B \\ a_{21}B & a_{22}B & \cdots & a_{2n}B \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1}B & a_{n2}B & \cdots & a_{nn}B \end{bmatrix}$$

(78)

If $A$ is $m$ dimensional and $B$ is $n$ dimensional, then obviously $A \otimes B$ is of dimensionality $mn$.

Consider now an operator in the space of $\psi$ defined as follows:

$$Z_k \psi_\alpha = \sigma_k \psi_\alpha$$

(79)

so that the $2^N$ eigenvalues of $Z_k$ are $\pm 1$, each being $2^{N-1}$ fold degenerate.
A suitable representation of $Z_k$ in the space of the $2^N$-dimensional state vectors $\psi$ is as follows:

$$Z_k = I \otimes I \otimes \cdots \otimes I \otimes Z \otimes I \otimes \cdots \otimes I$$

(80)

The $I$'s here are $2 \times 2$ identity matrices, while the operator $Z$ is the one defined by equation (71) and (73). One readily verifies that this representation satisfies the definition:

$$Z_k \psi = (I \otimes \cdots \otimes I \otimes Z \otimes I \otimes \cdots \otimes I)$$

$$\cdot (\mu_1^\alpha \otimes \cdots \otimes \mu_{k-1}^\alpha \otimes \mu_k^\alpha \otimes \mu_{k+1}^\alpha \otimes \cdots \otimes \mu_N^\alpha)$$

$$= \mu_1^\alpha \otimes \cdots \otimes \mu_{k-1}^\alpha \otimes Z \mu_k^\alpha \otimes \mu_{k+1}^\alpha \otimes \cdots \otimes \mu_N^\alpha$$

$$= \mu_1^\alpha \otimes \cdots \otimes \mu_{k-1}^\alpha \otimes \sigma_k \mu_k^\alpha \otimes \mu_{k+1}^\alpha \otimes \cdots \otimes \mu_N^\alpha$$

$$= (\sigma_k) \mu_1^\alpha \otimes \cdots \otimes \mu_{k-1}^\alpha \otimes \mu_k^\alpha \otimes \mu_{k+1}^\alpha \otimes \cdots \otimes \mu_N^\alpha$$

$$= \sigma_k \psi$$

where use was made of the identity:

$$(A \otimes B)(C \otimes D) = AC \otimes BD$$

(82)

which follows directly from the definition (78). $Z_k$ is thus, in this representation, a $2^N$-dimensional spinor. The corresponding definitions of the other operators that will be needed are:
\[ x_k | \mu_1^\alpha, \ldots, \mu_k^\alpha, \ldots, \mu_N^\alpha \rangle = | \mu_1^\alpha, \ldots, \mu_k^\beta, \ldots, \mu_N^\alpha \rangle \quad (83a) \]

where if \( \mu_k^\alpha = \mu_k^+ \), then \( \mu_k^\beta = \mu_k^- \), and if \( \mu_k^\alpha = \mu_k^- \), then \( \mu_k^\beta = \mu_k^+ \). The \( 2^N \) dimensional representation of \( x_k \) is:

\[ x_k = I \otimes I \otimes \cdots \otimes I \otimes X \otimes I \otimes \cdots \otimes I \]
\[ \uparrow \text{ kth factor} \quad (83b) \]

For the third operator the definition of \( y_k \) is again the obvious extension of (74b). Its \( 2^N \)-dimensional representation is:

\[ y_k = I \otimes \cdots \otimes I \otimes Y \otimes I \otimes \cdots \otimes I \]
\[ \uparrow \text{ kth factor} \quad (84) \]

The properties of these operators are

\[ [x_k, y_\ell]_+ = [x_k, z_\ell]_+ = [y_k, z_\ell]_+ = 0 \quad (\text{all } k \text{ and } \ell) \quad (85a) \]

\[ [x_k, y_\ell]_- = 2iz_k \delta_{k, \ell}; \quad [x_k, x_\ell]_- = 0 \quad (85b) \]

\[ [y_k, z_\ell]_- = 2ix_k \delta_{k, \ell}; \quad [y_k, y_\ell]_- = 0 \]

\[ [z_k, x_\ell]_- = 2iy_k \delta_{k, \ell}; \quad [z_k, z_\ell]_- = 0 \]

\[ x_k^2 = y_k^2 = z_k^2 = I \quad (85c) \]
for all $k$, where $I$ is the $2^N$-dimensional identity. Before we can proceed, it is necessary to give these operators the same periodicity as the space lattice has. Consequently we require that

$$X_{k+N} = X_k; \quad Y_{k+N} = Y_k; \quad Z_{k+N} = Z_k.$$  \hspace{1cm} (85d)

Consider now the following exponential operator acting on the state vector:

$$\exp(\theta Z_k)\psi = \sum_{r=0}^{\infty} \frac{\theta^r}{r!} Z_k^r \psi.$$  \hspace{1cm} (86a)

$$= (\cosh \theta + Z_k \sinh \theta) \psi$$

$$= [\cosh \theta + \sigma_k \sinh \theta] \psi$$

$$= \exp(\theta \sigma_k) \psi$$

where the usual series definition of the exponential matrix has been used, together with equation (79) and the fact that $\sigma_k^{2^r} = 1$, ($r = 0, 1, 2, \ldots$). Hence we have the desired result:

$$\exp(\theta Z_k)\psi = \exp(\theta \sigma_k) \psi.$$  \hspace{1cm} (86b)

In the same way one can show also that the following identity holds:

$$\exp(\theta Z_{k+L}) \psi = \exp(\theta \sigma_k \sigma_L) \psi.$$  \hspace{1cm} (87)
Observe now that

\[ \exp(\theta_1 Z_k Z_m) \exp(\theta_2 Z_k Z_n) = \exp((\theta_1 Z_k Z_m + \theta_2 Z_k Z_n)) \]  

(83)

since \( Z_k Z_m \) and \( Z_m Z_n \) commute. The proof of this is well-known and straightforward.*21 Using this we find that:

\[ \exp\left( \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \right) \psi_{\alpha} = \exp\left( \sum_{r=1}^{N} \sum_{s=1}^{N} \sigma \sigma_{r+s} \right) \psi_{\alpha} \]  

(89)

Each \( \psi_{\alpha} \) represents one of the possible states of the system, i.e. it represents one particular choice of the cell parameters \( \sigma \). Since each cell can be in one of two states and there are \( N \) cells, it follows that there are \( 2^N \) distinct state vectors \( \psi \). These are, of course, linearly independent, i.e.

\[ \sum_{\alpha=1}^{2^N} C_{\alpha} \psi_{\alpha} = 0 \Rightarrow C_{\alpha} = 0, \forall \alpha \]  

(90)

as is shown readily by induction. Thus we find that there exists a one-to-one correspondence between the terms of the sum \( \sum \) and the state vectors \( \psi_{\alpha} \). Making use of these results we can write the

---

*Let \( F(\lambda) = \exp(\lambda A) \exp(\lambda B) \exp(-1/2 \lambda C) \) where \( C = [A, B] \) is a C-number, not an operator. Then \( \partial F / \partial \lambda = (A+B-1/2C)F + [F, B] \). Then \( \exp(\lambda A)B - B\exp(\lambda A) = \sum_{n=0}^{\infty} \lambda^n (A^n B - B A^n) = \sum_{n=0}^{\infty} \lambda^n (A^n B - A^n B A^{-1} + C A^{-1} + 1) = \cdots = C A \sum_{n=1}^{\infty} \frac{\lambda^{n-1}}{(n-1)!} A^{n-1} = C \lambda \exp(\lambda A) \), so that \( [F, B] = \lambda C F \). Hence \( \partial F / \partial \lambda = (A+B-1/2C + \lambda C)F \). Then \( F(\lambda) = \exp(\lambda(A+B-1/2C + 1/2 \lambda C)) \) and \( F(1) = \exp(A+B) \). Consequently, \( \exp(A+B) = \exp(A) \exp(B) \exp(-1/2 \cdot [A, B]) \).
partition function in matrix form as follows:

\[ Q = A \sum_{\alpha=1}^{2N} \psi_{\alpha}^+ \exp\left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta^s + v \sum_{r=1}^{N} Z_r \right\} \psi_{\alpha} \]

(91)

where \( \psi_{\alpha}^+ = \psi_{\alpha}^* \) is the hermitian conjugate vector. Since all the elements of \( \psi \) are real, one notes that \( \psi_{\alpha}^+ = \psi_{\alpha}^* \).

If one defines a matrix \( S \) as follows:

\[ S = S_1 S_2 \]

(92)

where

\[ S_1 \exp\left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta^s \right\} = \prod_{r=1}^{N} \exp\left\{ \sum_{s=1}^{N} Z_r Z_{r+s} \theta^s \right\} \]

(93a)

\[ = \prod_{r=1}^{N} S_{1r} \]

\[ S_2 = \exp\left\{ v \sum_{r=1}^{N} Z_r \right\} = \prod_{r=1}^{N} \exp\left\{ v Z_r \right\} = \prod_{r=1}^{N} S_{2r} \]

(93b)

Then equation (91) can be rewritten:

\[ Q = A \sum_{\alpha=1}^{2N} \psi_{\alpha}^+ S \psi_{\alpha} \]

(94a)

\[ = \text{Tr}(S) \]

(94b)

\[ = \sum_{k=1}^{2N} \lambda_k \]

(94c)
Here $\text{Tr}(S)$ means "trace of the operator $S$" and $\lambda_k$ is the $k$th eigenvalue of $S$. Thus the problem resolves itself into one of determining the eigenvalues of $S$.

Before proceeding with the general theory it is perhaps well to illustrate the matrix formulation of the problem with a specific example and to demonstrate how it provides a convenient method for computing explicitly the partition functions for small $N$. Consider the case $N=4$. Here the basis vectors are

$$\psi_\alpha = \mu_1^\alpha \otimes \mu_2^\alpha \otimes \mu_3^\alpha \otimes \mu_4^\alpha$$

$$= \begin{pmatrix}
\mu_11^1
& \mu_21^1
& \mu_31^1
& \mu_41^1

\mu_11^2
& \mu_21^2
& \mu_31^2
& \mu_41^2

\mu_11^3
& \mu_21^3
& \mu_31^3
& \mu_41^3

\mu_11^4
& \mu_21^4
& \mu_31^4
& \mu_41^4

\vdots

\mu_12
& \mu_22
& \mu_32
& \mu_42
\end{pmatrix}$$

where the notation $\mu_1 = \begin{pmatrix} \mu_{11} \\ \mu_{12} \end{pmatrix}$ has been used. $\psi_\alpha$, then, is a $1 \times 16$ vector. Typical examples are:

$$\psi_1 = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = |+, +, +, +>$$

$$\psi_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = |+, +, +, ->$$
The matrix $S_1$ has the form:

$$S_1 = \exp\{(\theta_1+\theta_3)(Z_1Z_2+Z_2Z_3+Z_3Z_4+Z_4Z_1)+2\theta_2(Z_1Z_3+Z_2Z_4)\}$$

$$= \exp\{2\theta_1(Z_1Z_2+Z_2Z_3+Z_3Z_4+Z_4Z_1)+2\theta_2(Z_1Z_3+Z_2Z_4)\}$$

Writing now the diagonal elements of a matrix in the following form:

$$\begin{pmatrix}
A & 0 \\
B & \\
C & = \{A, B, C, D, \cdots\} \\
D & \\
0 & \\
\end{pmatrix}$$
we find that

\[ Z_1Z_2 + Z_2Z_3 + Z_3Z_4 + Z_4Z_1 \]

\[ = \begin{cases} I, & I, & -I, & -I, & -I, & I, & I \\ I, & -I, & I, & -I, & -I, & I, & I \end{cases} \]


\[ = \{4, 0, 0, 0, 0, 0, 0, -4, 0, 0, 0, 0, 0, 0, 0, 4\} \]

\[ Z_1Z_3 + Z_2Z_4 \]

\[ = \begin{cases} I, & -I, & I, & -I, & -I, & I, & I \end{cases} \]

\[ + \begin{cases} Z, & Z, & -Z, & -Z, & Z, & Z, & -Z, & -Z \end{cases} \]

\[ = \{2, 0, 0, -2, 0, 2, -2, 0, 0, -2, 2, 0, -2, 0, 0, 2\} \]

where the I's and Z's are 2x2 matrices defined as before. Now, for a diagonal matrix D one has:

\[ \exp(D) = \sum_{k=0}^{\infty} \frac{1}{k!} D^k = \sum_{k=0}^{\infty} \frac{1}{k!} \begin{pmatrix} \lambda_1^k & 0 \\ 0 & \lambda_2^k \end{pmatrix} \]

\[ \cdots \]

\[ \begin{pmatrix} \cdots & \cdots & \cdots \\ 0 & \cdots & \lambda_N^k \end{pmatrix} \]
\[
\begin{bmatrix}
\sum_{k_1=0}^{\infty} \frac{\lambda_1^{k_1}}{k_1!} & 0 \\
& \sum_{k_2=0}^{\infty} \frac{\lambda_2^{k_2}}{k_2!} & 0 \\
& & \ddots & \ddots \\
& & & \sum_{k_N=0}^{\infty} \frac{\lambda_N^{k_N}}{k_N!}
\end{bmatrix}
\]

\[
\begin{bmatrix}
\exp(\lambda_1) \\
\exp(\lambda_2) \\
\vdots \\
\exp(\lambda_N)
\end{bmatrix}
= \begin{bmatrix}
0 \\
\exp(\lambda_2) \\
\vdots \\
\exp(\lambda_N)
\end{bmatrix}
\]

Therefore:

\[
S_1 = \begin{bmatrix}
\exp(8\theta_1) & 0 & \exp(4\theta_2) & 0 \\
1 & 1 & 1 & 1 \\
1 & \exp(-8\theta_1) & \exp(4\theta_2) & \exp(-4\theta_2) \\
1 & 1 & \exp(-8\theta_1) & \exp(4\theta_2) \\
1 & 1 & \exp(-8\theta_1) & \exp(4\theta_2) \\
0 & \exp(8\theta_1) & 0 & \exp(4\theta_2)
\end{bmatrix}
\]

\[(95)\]
Finding $S_2$ in the same way, one obtains:

$$
S = \begin{pmatrix}
\exp\{4(2\theta_1+\theta_2)\} & 0 \\
\exp\{2\nu\} & \\
\exp\{2\nu\} & \\
\exp\{-4\theta_2\} & \\
\exp\{4(-2\theta_1+\theta_2)\} & \\
\exp\{-4\theta_2\} & \\
\exp\{-4\theta_2\} & \\
\exp\{2\nu\} & \\
\exp\{-4\theta_2\} & \\
\exp\{4(-2\theta_1+\theta_2)\} & \\
\exp\{-2\nu\} & \\
\exp\{-4\theta_2\} & \\
\exp\{-4\theta_2\} & \\
\exp\{-2\nu\} & \\
\exp\{-2\nu\} & \\
0 & \exp\{4(2\theta_1+\theta_2)\}
\end{pmatrix}$$

(96)
Consequently:

\[
\text{Tr}(S) = 2\exp\{4(2\theta_1+\theta_2)\}[\cosh(4v)+4\exp\{-4(2\theta_1+\theta_2)\}\cosh 2v+2\exp\{-8(\theta_1+\theta_2)\}
\]

\[+\exp\{-16\theta_1\}] \tag{97}\]

\[
=\begin{cases} 
A^{-1}Q_4 & \text{(fluid)} \\
Q_4 & \text{(ferromagnet)}
\end{cases}
\]

Partition functions for low N derived in essentially this way are tabulated in Appendix I. While one can simplify the process by taking advantage of the symmetries of these matrices, the procedure becomes too tedious for \( N > 9 \).

Addressing ourself once more now to the general problem of obtaining a mathematically tractable, preferably closed-form, expression for the partition function, one can start either directly from the matrix formulation in equation (91) or one can proceed from equation (94c). In taking the former route first, we consider the simplest case where \( v = 0 \), so that \( S_2 = 1 \) (1 here is the \( 2^N \)-dimensional identity). We define now an operator \( n \) as follows:

\[
\eta_{k\ell} = Z_k Z_{k+\ell} \tag{98}\]

Noting that

\[
[\eta_{k\ell}, \eta_{mn}]_+ = 0
\]

for all \( k, \ell, m, \) and \( n \), and taking advantage of the following identity, which follows in the same way as equation (86):
we can write $S_1$ in the following form:

$$S_1 = \exp\left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta_s \right\}$$

$$= \prod_{r=1}^{N} \prod_{s=1}^{N} (\cosh \theta_s + n_{rs} \sinh \theta_s)$$

The principal part of the partition function can then be written in the following way:*

$$Q = \text{Tr}(S) = \text{Tr}(S_1)$$

$$(\nu=0)$$

$$= \text{Tr}\left\{ \prod_{r=1}^{N} \prod_{s=1}^{N} (\cosh \theta_s + n_{rs} \sinh \theta_s) \right\}$$

$$= \prod_{s=1}^{N} \cosh \theta_s \prod_{r=1}^{N} \prod_{s=1}^{N} (I + n_{rs} \tanh \theta_s)$$

where the following obvious identity was used:

$$\text{Tr}(cA) = c \text{Tr}(A)$$

in which $c$ is a number (scalar) and $A$ is a matrix (operator). Writing now

$$\omega_k = \tanh \theta_k$$

*It is assumed in what follows that $N$ is odd.
we have:

\[
Q(v=0) = \left[ \prod_{k=1}^{N} \cosh^{N} \theta_{k} \right] \text{Tr} \left\{ I + \sum_{r=1}^{N} \sum_{s=1}^{N} \eta_{rs} \omega_{s} \right\} (104)
\]

\[
+ \frac{1}{2!} \sum_{r_{1}=1}^{N} \sum_{r_{2}=1}^{N} \sum_{s_{1}=1}^{N} \sum_{s_{2}=1}^{N} \eta_{r_{1}s_{1}} \eta_{r_{2}s_{2}} \omega_{s_{1}} \omega_{s_{2}} \]

\[
+ \cdots + \frac{1}{n!} \sum_{r_{1}=1}^{N} \cdots \sum_{r_{n}=1}^{N} \sum_{s_{1}=1}^{N} \cdots \sum_{s_{n}=1}^{N} \eta_{r_{1}s_{1}} \cdots \eta_{r_{n}s_{n}} \omega_{s_{1}} \cdots \omega_{s_{n}} \]

\[
+ \cdots \}
\]

the prime on the summation indicating that in any given term of the sum each particular \( \eta_{rs} \) may occur only once (considering \( \eta_{rs} \) and \( \eta_{sr} \) as being distinct).

Since

\[
\text{Tr}(A+B) = \text{Tr}(A) + \text{Tr}(B)
\]

and observing that \( \text{Tr}(I) = 2^{N} \), we have:

\[
Q(v=0) = \left[ \prod_{k=1}^{N} \cosh^{N} \theta_{k} \right] \left\{ 2^{N} + \text{Tr} \left( \sum_{r=1}^{N} \sum_{s=1}^{N} \eta_{rs} \omega_{s} \right) \right\} (105)
\]

\[
+ \cdots + \frac{1}{n!} \text{Tr} \left( \sum_{r_{1}=1}^{N} \cdots \sum_{r_{n}=1}^{N} \sum_{s_{1}=1}^{N} \cdots \sum_{s_{n}=1}^{N} \eta_{r_{1}s_{1}} \cdots \eta_{r_{n}s_{n}} \omega_{s_{1}} \cdots \omega_{s_{n}} \right)
\]

\[
+ \cdots \}
Now

\[ \text{Tr}(\eta_{rs}) = \text{Tr}(Z_r Z_{r+s}) = \begin{cases} 0 & (s \neq 0) \\ 2^N & (s = 0) \end{cases} \]

The non-zero result is trivial, however, since for \( s = 0, \theta_s = 0 \), and thus \( \omega_s = 0 \), so that \( \text{Tr}(\eta_{rs} \omega_s) = 0 \) also. The fact that \( \text{Tr}(Z_r Z_{r+s}) = 0 \) for \( s \neq 0 \) is directly obvious from the fact that:

\[ \text{Tr}(A \Theta B) = \text{Tr}(A) \text{Tr}(B) \]

Hence:

\[ \text{Tr}(\eta_{rs}) = \text{Tr}(Z_r Z_{r+s}) = 2^{N-2} \text{Tr}(Z) \text{Tr}(Z) = 0 \quad (r \neq s) \]

Consequently all terms in \( Q \) with unpaired \( n \)'s make a zero contribution. The only non-vanishing terms are those involving products of \( n \)'s yielding an identity. Since the \( n \)'s cannot be repeated in any product, we find that:

\[ Q(v=0) = [2^N \sum_{k=1}^N \cosh^{N} \theta_k] [1 + 1/2! \sum_{r_1=1}^N \sum_{r_2=1}^N \sum_{s_1=1}^N \sum_{s_2=1}^N (\delta_{r_1, r_2} \delta_{r_1+s_1, r_2} \omega_{s_1} \omega_{s_2})] \]

\[ +1/3! \sum_{r_1=1}^N \sum_{r_2=1}^N \sum_{r_3=1}^N \sum_{s_1=1}^N \sum_{s_2=1}^N \sum_{s_3=1}^N (\delta_{r_1, r_2} \delta_{r_1+s_1, r_2+s_2} \omega_{s_1} \omega_{s_2} \omega_{s_3}) \]

\[ + \cdots \]
The δ-products in each term are all possible permutations of subscripts such that all subscripts are paired and no n is repeated identically.

The multiplicity of succeeding terms obviously increases rapidly and the labor of carrying out this type of expansion becomes considerable after the first few terms, partaking of most of the difficulties of carrying out cluster-integral expansions. As in the latter case, graphic techniques are possible so that the problem becomes one of topology rather than algebraic analysis.

To do so in the present case, a slight change in notation is helpful. Let

\[ \rho_{rs} = Z_r Z_s \]  

then

\[ S_1 = \exp \left( \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta_{rs} \right) = \exp \left( \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{s} \theta_{rs} \right) = \exp \left( \sum_{r=1}^{N} \sum_{s=1}^{N} \rho_{rs} \theta_{rs} \right) \]

\[ Q(\nu=0) = \left[ \prod_{k=1}^{N} \cosh \theta_k \right] [Z^N + \text{Tr} \sum_{r=1}^{N} \sum_{s=1}^{N} \rho_{rs} \omega_{rs} \omega_{rs}] \]

\[ + \cdots + 1/n! \text{Tr} \sum_{r_1=1}^{N} \cdots \sum_{r_n=1}^{N} \sum_{s_1=1}^{N} \cdots \sum_{s_n=1}^{N} \rho_{r_1 s_1} \cdots \rho_{r_n s_n} \omega_{r_1-s_1} \omega_{r_1-s_1} \cdots \omega_{r_n-s_n} \]

\[ \cdots \]

The factor \( \rho_{rs} \omega_{rs} \) gives the contribution to the partition function due to the interaction between the rth and sth cell. One may therefore think of \( \rho_{rs} \) as a bond between these two cells and of \( \omega_{rs} \) as determining the strength of this bond. From this point of view, then, the nonzero contributions form closed polygons. All open figures and closed figures with open
branches become zero upon taking the trace.* Figure 8 shows typical zero and nonzero contributions.

Typical Nonvanishing Configurations  
Typical Vanishing Configurations

(a)  
(b)  

Figure 8. Typical Graphs Showing Vanishing and Nonvanishing Contributions

One can, of course, assign a direction to these bonds, for example from the first index toward the second one. In that case one can say that no bond may be repeated in any nonzero figure. The cells in Figure 8 are displayed in two dimensions; this is only for convenience in displaying the bonds and has no bearing on the dimensionality of the model.

In terms of such graphs the partition function may then be written as follows:

*Open figures or closed polygons with open branches contain unpaired $\rho$'s. By the same argument as that following equation (105) such terms make a vanishing contribution to the partition function. One may observe that $\rho_{ii} = I$, so that $\text{Tr}(\rho_{ii}) = 2^N$; however, we do not permit self-interactions of cells with themselves so that such terms are excluded.
\[ Q(v=0) = \left[ 2^N \prod_{k=1}^{N} \cosh^N(\theta_k) \right] \left[ 1 + \sum_{\{n\}} \Omega_n \right] \]

where \( \sum_{\{n\}} \) means sum over all figures with \( n \) sides, and \( \Omega_n \) represents the appropriate product of \( \omega \)'s corresponding to nonzero figures of this type.

This method of solution is quite suitable to determine the first few terms of the partition function, and can be considered then as a low-temperature approximation since only the interactions of small numbers of particles are included. If one wishes to include terms involving larger clusters, the process rapidly becomes very tedious and poses vexing topological problems. Furthermore, one must remember that the assumption \( v=0 \) eliminated the matrix \( S_2 \). For the solution of the general problem, \( S_2 \) must be included. It can be treated very much in the same way as \( S_1 \); but of course this adds additional complications. One other difficulty that has been ignored in this analysis is the periodic boundary conditions. If \( N \) is very large, this is a trivial matter; but for systems of finite size these boundary conditions, which are essential to the matrix formulation, result in additional non-zero configurations which increase the complexity of the topological problem considerably.

An alternative method of finding a solution of the problem by matrix methods starts from equation (94) and involves determining the eigenvalues of the operators \( S \) by attempting to establish a homomorphism between \( S \) and the group of orthogonal rotations. If this were possible, the eigenvalues of the rotation operators involved could readily be determined so that the corresponding eigenvalue spectrum of \( S \) could be deduced. The method, which is an application and extension of the Onsager-Kaufman formalism to the present problem, is explored in detail in Appendix 2.17,19

The analysis there shows that in the present problem, where all interactions
are active, the simplifications that are possible in solving the two-dimensional Ising problem can no longer be made. It is found that the operator $S$ is not the spin representative of commuting rotations as is the case in the two-dimensional nearest-neighbor model. Instead it is found to be associated with a tensor transformation. No simple relationship appears to exist between the eigenvalues of that transformation and those of $S$. Indeed, the problem contains all the difficulties of the three-dimensional Ising problem which has also not yet been solved by the matrix method.

The next chapter will therefore develop a different approach that does lead to a meaningful and useful series solution of the present problem which holds for all values of the activity.*

*For the purpose of this paper we define the activity as (cf. equation (36)) $y = \exp(2\nu)$
CHAPTER IV
EVALUATION OF THE PARTITION FUNCTION

A. General

The methods of evaluating the partition function examined in the last chapter, while of considerable interest in themselves, do not appear to offer any complete solution of the problem. A different approach will therefore be adopted in this chapter which leads to a useful series formulation of the partition function, valid for all values of the chemical potential or external magnetic field.

The starting point of the present method is again the partition function as formulated in the last chapter (cf. equations (91) through (94)):

\[
Q = A \sum_{\alpha=1}^{2^N} \psi_\alpha^\dagger \exp \left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta + \nu \sum_{r=1}^{N} Z_r \right\} \psi_\alpha
\]

\[
= A \mathrm{Tr} \{ \exp \left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta + \nu \sum_{r=1}^{N} Z_r \right\} \}
\]

where

\[
A = \begin{cases} 
\exp\{N(\nu-\theta)\} & \text{(fluid)} \\
1 & \text{(ferromagnet)} 
\end{cases}
\]

\[
Q = \begin{cases} 
Q_N & \text{(fluid)} \\
Q_N & \text{(ferromagnet)} 
\end{cases}
\]

To proceed, let us consider the simplest case first.
B. The Case \( v=0 \)

The partition function to be evaluated, if \( v=0 \), is:

\[
Q(v=0) = \operatorname{ATr}\left\{ \exp\left( \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta_s \right) \right\}
\]  

\( (112) \)

Let us analyze the quadratic form appearing in the exponent, which can be expressed as follows:

\[
U = \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta_s \]  

\( (113) \)

\[
= \zeta^\dagger \phi \zeta
\]

where \( \zeta \) is an \( N \)-dimensional vector defined by:

\[
\zeta = |Z_1, Z_2, \ldots, Z_N>
\]  

\( (114) \)

while \( \phi \) (not to be confused with the \( \phi \) of equation (18)) is an \( N \times N \) matrix:

\[
\phi = \begin{bmatrix}
0 & \theta_1 & \theta_2 & \theta_3 & \cdots & \theta_{N-2} & \theta_{N-1} \\
\theta_{N-1} & 0 & \theta_1 & \theta_2 & \cdots & \theta_{N-3} & \theta_{N-2} \\
\theta_{N-2} & \theta_{N-1} & 0 & \theta_1 & \cdots & \theta_{N-4} & \theta_{N-3} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\theta_1 & \theta_2 & \theta_3 & \theta_4 & \cdots & 0 & \theta_{N-1}
\end{bmatrix} = \begin{bmatrix}
0 & \theta_1 & \theta_2 & \theta_3 & \cdots & \theta_2 & \theta_1 \\
\theta_1 & 0 & \theta_1 & \theta_2 & \cdots & \theta_3 & \theta_2 \\
\theta_2 & \theta_1 & 0 & \theta_1 & \cdots & \theta_4 & \theta_3 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\theta_1 & \theta_2 & \theta_3 & \theta_4 & \cdots & 0 & \theta_1
\end{bmatrix}
\]  

\( (115a) \)

where use was made of the fact that \( \theta_{N-r}^{\dagger} = \theta_r \) (see equations (17) and (36)).

This can also be written:

\[
\theta_{ij} = \theta_{j-i}
\]  

\( (115b) \)

remembering that by definition \( \theta_0=0 \). Thus \( \phi \) is a doubly cyclic matrix.
Now let $\omega_k$ be the $k$th of the $N$ roots of unity, i.e.:

$$\omega_k = \exp\{i(2\pi/N)k\} \quad (k = 0, 1, 2, \ldots) \quad (116)$$

We can then define a vector as follows:

$$\overline{V}_k = |\omega_k^0, \omega_k^1, \omega_k^2, \ldots, \omega_k^{N-1}> \quad (117a)$$

i.e.

$$\overline{V}_{k\ell} = \omega_k^{\ell-1} = \exp\{i(2\pi/N)k(\ell-1)\} \quad (117b)$$

Then:

$$\phi \overline{V}_k = \begin{bmatrix}
0_1 & \omega_k^1 + \theta_2 \omega_k^2 + \ldots + \theta_{N-1} \omega_k^{N-1} \\
0_{N-1} & \omega_k^0 + \theta_1 \omega_k^2 + \ldots + \theta_3 \omega_k^{N-2} + \theta_2 \omega_k^{N-1} \\
& \vdots \\
0_1 & \omega_k^0 + \theta_2 \omega_k^1 + \ldots + \theta_{N-3} \omega_k^{N-2} + \theta_1 \omega_k^{N-1}
\end{bmatrix} = \lambda_k \overline{V}_k \quad (118)$$

where:

$$\lambda_k = (\omega_k^1 + \omega_k^{N-1}) \theta_1 + (\omega_k^2 + \omega_k^{N-2}) \theta_2 + \ldots \quad (119)$$

$$= 2 \sum_{r=1}^{[N/2]} \cos\left(\frac{2\pi k r}{N}\right) \theta_r (1-1/2^r, N/2)$$

$$= \sum_{r=1}^N \cos\left(\frac{2\pi k r}{N}\right) \theta_r$$

since $\omega_k^r + \omega_k^{N-r} = 2\cos\left(\frac{2\pi k r}{N}\right)$. Here $[N/2]$ designates the largest integer $\leq N/2$. 
The factor \((1-1/2^r, N/2)\) prevents double counting of the \((r/2)\)th term when \(N\) is even.

The \(\lambda_k\)'s are thus the eigenvalues of \(\Phi\). Since \(\Phi\) is a real and symmetric matrix, all its eigenvalues are of course real, as is also apparent from (119). Indeed, the eigenvalues of \(\Phi\) are the finite Fourier cosine transform of the potential. In order to normalize the eigenvectors of \(\Phi\), we note that

\[
\langle \psi_k | \psi_{\ell} \rangle = \sum_{r=1}^{N} \exp\{-i(2\pi/N)k(r-1)\} \exp\{i(2\pi/N)\ell(r-1)\}
\]

(120)

\[
= \sum_{r=1}^{N} \exp\{i(2\pi/N)(\ell-k)r\} = N \delta_{k, \ell}
\]

The last equality can readily be proved by considering that \(\omega_N = \exp\{2\pi i\} = 1\). Hence

\[
(1-\omega_N) = (1-\omega_1)(1+\omega_1+\omega_1^2+\cdots+\omega_1^{N-1})
\]

\[
= (1-\omega_1) \sum_{r=0}^{N-1} \omega_r = 0
\]

But \(\omega_1 = \exp\{i \pi/N\} \neq 1\). Hence

\[
\sum_{r=0}^{N-1} \omega_r = \sum_{r=1}^{N} \omega_r = 0
\]

(121)

The \(N\) \(N\)th roots of unity form a group. Therefore taking the \(a\)th power of all group elements results merely in an automorphism of the group.
Equation (121) tells us that the sum of all group elements vanishes; then also:

\[\sum_{r=1}^{N} \omega_{kr} = \sum_{r=1}^{N} \exp\{i(2\pi/N)kr\} = \sum_{r=1}^{N} \omega_{kr} = 0 \quad (122)\]

Equation (120) then follows.

The normalized eigenvectors of \( \Phi \) are consequently

\[V_{k} = 1/\sqrt{N} |1, \omega_{k}, \omega_{k}^{2}, \ldots, \omega_{k}^{N-1}\rangle \quad (123)\]

Knowing the eigenvectors of \( \Phi \), it is of course possible now to diagonalize that matrix. To that end let us construct a matrix \( S \) having the eigenvectors of \( \Phi \) as its columns:

\[S = \begin{pmatrix} V_{1} & V_{2} & \cdots & V_{N} \end{pmatrix} \quad (124)\]

or:

\[S_{k\ell} = V_{k\ell} \quad (125)\]

where \( V_{k\ell} \) is the \( \ell \)th component of the eigenvector \( V_{k} \). We observe that

\[S^\dagger S = \begin{pmatrix} \langle V_{1}|V_{1}\rangle & \langle V_{1}|V_{2}\rangle & \cdots & \langle V_{1}|V_{N}\rangle \\ \langle V_{2}|V_{1}\rangle & \langle V_{2}|V_{2}\rangle & \cdots & \langle V_{2}|V_{N}\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle V_{N}|V_{1}\rangle & \langle V_{N}|V_{2}\rangle & \cdots & \langle V_{N}|V_{N}\rangle \end{pmatrix} = I \quad (126)\]
since \( \langle \psi_k | \psi_\ell \rangle = \delta_{k, \ell} \). Thus we find that \( S^\dagger = S^{-1} \), i.e. \( S \) is a unitary matrix.

Let us now perform a similarity transformation on \( \phi \):

\[
S^\dagger \phi S = \begin{pmatrix}
V_1^* \\
V_2^* \\
\vdots \\
V_N^*
\end{pmatrix}
\begin{pmatrix}
\lambda_1 V_1 & \lambda_2 V_2 & \cdots & \lambda_N V_N \\
\vdots & \vdots & & \vdots \\
\vdots & \vdots & & \vdots \\
\vdots & \vdots & & \vdots \\
\end{pmatrix}
\]

(127)

\[
= \begin{pmatrix}
\lambda_1 \langle \psi_1 | \psi_1 \rangle & \lambda_2 \langle \psi_1 | \psi_2 \rangle & \cdots & \lambda_N \langle \psi_1 | \psi_N \rangle \\
\lambda_1 \langle \psi_2 | \psi_1 \rangle & \lambda_2 \langle \psi_2 | \psi_2 \rangle & \cdots & \lambda_N \langle \psi_2 | \psi_N \rangle \\
\vdots & \vdots & & \vdots \\
\lambda_1 \langle \psi_N | \psi_1 \rangle & \lambda_2 \langle \psi_N | \psi_2 \rangle & \cdots & \lambda_N \langle \psi_N | \psi_N \rangle \\
\end{pmatrix}
\]

\[
= \begin{pmatrix}
\lambda_1 & 0 \\
0 & \lambda_2 \\
\vdots & \vdots \\
0 & \lambda_N
\end{pmatrix} = D
\]

where \( D \) is a diagonal matrix having the eigenvalues of \( \phi \) on its main diagonal. Thus if we define a vector \( \eta \) as follows:

\[
\zeta = S \eta
\]

(128)

we can diagonalize the quadratic form of equation (113):

\[
U = \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \theta_s
\]

(129)

\[
= \zeta^\dagger \phi \zeta = \eta^\dagger (S^\dagger \phi S) \eta
\]

\[
= \eta^\dagger D \eta = \sum_{r=1}^{N} \eta_r^* \eta_r \lambda_r = \sum_{r=1}^{N} |\eta_r|^2 \lambda_r
\]
The partition function is then:

\[ Q(v=0) = A \text{Tr} \left\{ \exp \left[ \sum_{r=1}^{N} |n_r|^{2} \lambda_r \right] \right\} \]  

(130)

We must remember that the \( n \)'s are in fact operators, i.e.:

\[ \eta_r = \sum_{s=1}^{N} r_s s^* Z_s = 1/\sqrt{N} \sum_{s=1}^{N} \exp \{-i(2\pi/N)r(s-1)\} Z_s \]  

(131)

Consequently we have, using equation (79):

\[ \eta_r \psi_\alpha = 1/\sqrt{N} \sum_{s=1}^{N} \exp \{-i(2\pi/N)r(s-1)\} Z_s \psi_\alpha \]  

(132)

= \frac{1}{\sqrt{N}} \sum_{s=1}^{N} \exp \{-i(2\pi/N)r(s-1)\} \sigma_s^\alpha \psi_\alpha = \chi_r^\alpha \psi_\alpha

\( \chi_r \) is thus the eigenvalue of the operator \( \eta_r \). We can then express the partition function in this way:

\[ Q(v=0) = A \sum_{\alpha=1}^{2^N} \psi_\alpha^+ \exp \left\{ \sum_{r=1}^{N} |n_r|^{2} \lambda_r \right\} \psi_\alpha \]

\[ = A \sum_{\alpha=1}^{2^N} \psi_\alpha^+ \exp \left\{ \sum_{r=1}^{N} |x_r^\alpha|^{2} \lambda_r \right\} \psi_\alpha \]

\[ = A \sum_{(c)} g(c) \exp \left\{ \sum_{r=1}^{N} |x_r(c)|^{2} \lambda_r \right\} \]
where the first sum is one over **all** configurations, i.e. all microstates, while the last sum is over all macroscopically distinct configurations, \( g(c) \) indicating the degeneracy of each configuration, i.e. the number of microstates corresponding to each macrostate.

Before proceeding to evaluate this sum, we must observe that

\[
\zeta^\dagger = n^\dagger S n^\dagger = <Z_1, Z_2, \ldots, Z_N|Z_1, Z_2, \ldots, Z_N> = N
\]

(134)

And similarly:

\[
\sum_{r=1}^{N} \chi_r^* \chi_r = \frac{1}{N} \sum_{r=1}^{N} \sum_{s=1}^{N} \sum_{t=1}^{N} \exp\{i(2\pi/N)(s-t)\} \sigma_s \sigma_t = N
\]

(135)

Equation (134) is a consistency condition that must be satisfied in performing the sum in equation (133). The geometrical significance of this condition can best be understood if we think of the original sum of the \( \sigma \)'s in the partition function as a sum along \( N \) coordinate axes from -1 to +1. The sum, then, defines the corners of an \( N \)-dimensional "cube". All corners are equidistant from the origin, this distance \( d \) being given by \( d^2 = \sum_{r=1}^{N} \sigma_r^2 = N \), so that \( d = \sqrt{N} \). There are altogether \( 2^N \) such corners (see Fig. 9 which shows the cube and corner coordinates for \( N=3 \)).
Figure 9. Corner Coordinates for 3-Dimensional Cube.

The similarity transformation, equations (128) and (129), is tantamount to a rotation of coordinate axes so as to diagonalize the quadratic form $U$.

The following table shows the coordinates of the corners of the cube in Figure 9 in the transformed coordinate system. Since the origin is, of course, not affected by this transformation, the distance to the corners remains invariant under the transformation. Hence the partition function must satisfy the consistency condition in the transformed coordinate system as well.

| Original Coordinate | $x_1$ | $|x_1|^2$ | $x_2$ | $|x_2|^2$ | $x_3$ | $|x_3|^2$ |
|---------------------|-------|----------|-------|----------|-------|----------|
| $(1,1,1)$           | 0     | 0        | 0     | 0        | $\sqrt{3}$ | 3        |
| $(1,1,-1)$          | $1/\sqrt{3}-i$ | $4/3$   | $1/\sqrt{3}+i$ | $4/3$     | $1/\sqrt{3}$ | $1/3$    |
TABLE 2 Continued

| Original Coordinate | $x_1$ | $|x_1|^2$ | $x_2$ | $|x_2|^2$ | $x_3$ | $|x_3|^2$ |
|---------------------|-------|-----------|-------|-----------|-------|-----------|
| $(1,-1,-1)$         | $2/\sqrt{3}$ | $4/3$ | $2/\sqrt{3}$ | $4/3$ | $-1/\sqrt{3}$ | $1/3$ |
| $(-1,1,1)$          | $-2/\sqrt{3}$ | $4/3$ | $-2/\sqrt{3}$ | $4/3$ | $1/\sqrt{3}$ | $1/3$ |
| $(-1,1,-1)$         | $-1/\sqrt{3}+i$ | $4/3$ | $-1/\sqrt{3}+i$ | $4/3$ | $-1/\sqrt{3}$ | $1/3$ |
| $(-1,-1,1)$         | $-1/\sqrt{3}+i$ | $4/3$ | $-1/\sqrt{3}-i$ | $4/3$ | $-1/\sqrt{3}$ | $1/3$ |
| $(-1,-1,-1)$        | $0$ | $0$ | $0$ | $0$ | $0$ | $-\sqrt{3}$ | $3$ |

In order to evaluate the sum in equation (133) let us first consider a system with all cells unoccupied. In that case we have:

$$x_r = 1/\sqrt{N} \sum_{s=1}^{N} \omega^r (s-1) \sigma_s = 1/\sqrt{N} \sum_{s=1}^{N} \exp\{-i(2\pi/N)r(s-1)\} \sigma_s$$  \hspace{1cm} (136)

$$= -1/\sqrt{N} \sum_{s=1}^{N} \omega^r (s-1) = -1/\sqrt{N} \left( \sum_{s=1}^{N} \omega (s-1) \right)^*$$

$$= \begin{cases} 0 & (r \neq N) \\ -\sqrt{N} & (r = N) \end{cases}$$

Here use has been made of equation (120) and the result proved in connection therewith. The star above indicates complex conjugation. Thus, if we choose as our macroscopic configurations the occupancy states of the system and indicate these as the argument of $x_r$ we can write the above result in the form:

$$|x_r(0)|^2 = \begin{cases} 0 & (r \neq N) \\ N & (r = N) \end{cases}$$  \hspace{1cm} (137)
This state is clearly non-degenerate, i.e. there is only one microstate corresponding to this macrostate. Let us next consider the state of full occupancy. This state is, of course, likewise non-degenerate. We have now that all σ's are +1 so that

\[ x_\tau = +1/\sqrt{N} \sum_{s=1}^{N} \omega^* r(s-1) \]

Thus we find that

\[ |x_\tau(N)|^2 = \begin{cases} 0 & (r \neq N) \\ N & (r = N) \end{cases} = |x_\tau(0)|^2 \]

Suppose next that only one cell is occupied, say the qth cell. Then:

\[ x_\tau = -1/\sqrt{N} \sum_{s=1}^{q-1} \omega^* r(s-1) + \sum_{s=q+1}^{N} \omega^* r(s-1)+1/\sqrt{N} \omega^* r(q-1) \]

\[ = -1/\sqrt{N} \sum_{s=1}^{N} \omega^* r(s-1)+2/\sqrt{N} \omega^* r(q-1) \]

\[ = \begin{cases} 2/\sqrt{N} \omega^* r(q-1) & (r \neq N) \\ 2/\sqrt{N} - \sqrt{N} & (r = N) \end{cases} \]

Hence:

\[ |x_\tau(1)|^2 = \begin{cases} 4/N & (r \neq N) \\ (N-2)^2/N & (r = N) \end{cases} \]
Again we find that if all but one of the cells are occupied we obtain the same result for \(|x_r|^2\), i.e.

\[ |x_r(N-1)|^2 = |x_r(1)|^2 \]  

Here the degeneracy is \(N\), and equation (140) is unaffected by which particular cell is occupied. If, next, we examine states with two cells occupied and suppose that these cells are the \(i\)th and \(j\)th one, then

\[
x_r = -1/\sqrt{N} \left[ \sum_{s=1}^{i-1} \omega^* r(s-1) + \sum_{s=i+1}^{j-1} \omega^* r(s-1) + \sum_{s=j+1}^{N} \omega^* r(s-1) \right]
\]

\[+1/\sqrt{N} [\omega^* r(i-1) + \omega^* r(j-1)]\]

\[= -1/\sqrt{N} \sum_{s=1}^{N} \omega^* r(s-1) + 2/\sqrt{N} [\omega^* r(i-1) + \omega^* r(j-1)]\]

\[= \begin{cases} 
2/\sqrt{N} [\omega^* r(i-1) + \omega^* r(j-1)] & \text{if } r\neq N \\
4/\sqrt{N} - \sqrt{N} & \text{if } r=N
\end{cases}\]

so that, for \(r\neq N\), we have:

\[ |x_r(2)|^2 = 4/N(\omega^* r(i-1) + \omega^* r(j-1)) (\omega^* r(i-1) + \omega^* r(j-1)) \]

\[= 4/N(2+\omega^* r(i-j) + \omega^* r(j-i))\]

\[= 4/N(2+2\cos[(2\pi/N)r(i-j)])\]

\[= 4/N \sum_{i=1}^{2} \sum_{j=1}^{2} \cos[(2\pi/N)r(q_i-q_j)] \quad (r\neq N)\]
where in the last equation \( q_i \neq i; q_j = j \). Thus

\[
|\chi_r(2)|^2 = \begin{cases} 
\left(\sum_{i=1}^{2} \sum_{j=1}^{2} \cos((2\pi/N)r(q_i-q_j))\right) \quad (r \neq N) \\
\frac{(N-4)^2}{N} \quad (r = N)
\end{cases}
\tag{145}
\]

We also find in this instance that:

\[
|\chi_r(N-2)|^2 = |\chi_r(2)|^2
\]

i.e. \( |\chi_r|^2 \) is invariant to a change in configuration from occupied cells to holes. The degeneracy of this state is, of course, \( \binom{N}{2} \); however, here \( |\chi_r|^2 \) depends upon the particular cells that are occupied (or empty).

By continuing the analysis in this way we find for a state with \( n \) cells occupied (or empty) that:

\[
|\chi_r(n)|^2 = \begin{cases} 
\left(\sum_{i=1}^{n} \sum_{j=1}^{n} \cos((2\pi/N)r(q_i-q_j))\right) \quad (r \neq N) \\
\frac{(N-2n)^2}{N} \quad (r = N)
\end{cases}
\tag{147}
\]

\[
= |\chi_r(N-n)|^2
\]

where \( 0 \leq n \leq \lfloor N/2 \rfloor \)

It was assumed here that the occupied (or empty) cells are cells \( q_i \) through \( q_j \). The total degeneracy of this state is \( \binom{N}{n} \), but as in the case \( n=2 \), it depends on the particular cells that are actually occupied (or empty).
We are now in a position to carry out the sum in equation (133), using as the macrostate configurations the total occupancy of the system. Before proceeding with this program we can check first that the consistency condition, equations (134) and (135), is indeed satisfied for any term in such an expansion. Thus consider the term corresponding to \( n \) occupied or \( (N-n) \) empty cells. For such a term we have:

\[
\sum_{r=1}^{N} |x_r(n)|^2 = \frac{4}{N} \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos\left(\frac{2\pi}{N} r(q_i - q_j)\right) + \frac{(N-2n)^2}{N}
\]

\[
= \frac{4}{N} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{r=1}^{N} \frac{1}{2} \left( w_r(q_i - q_j) + w_r(q_j - q_i) \right) + \frac{(N-2n)^2}{N}
\]

\[
= \frac{4}{N} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{r=1}^{N} N \delta_{i,j} - \frac{4n^2}{N} + \frac{4n^2}{N} - \frac{4n}{N}
\]

\[
= N
\]

Thus the consistency condition is satisfied in the proposed expansion. Equation (133) can then be expanded as follows:

\[
Q(v=0) = A \sum_{\{C\}} g(c) \exp\{ \sum_{r=1}^{N} |x_r(c)|^2 \lambda_r \}
\]

\[
= 2A \{ \exp\{ \sum_{r} |x_r(0)|^2 \lambda_r \} + N \exp\{ \sum_{r} |x_r(1)|^2 \lambda_r \} + \cdots \}
\]

\[
+ \sum_{q_1=1}^{N} \sum_{q_2=1}^{N} \exp\{ \sum_{r} |x_r(q_1, q_2)|^2 \lambda_r \} + \cdots \}
\]

\((q_1 < q_2)\)
Here the factor 2 results from the symmetry of the partition function with respect to occupied states and holes (see equation (147)). The sum in equation (149) goes to the \([N/2]nd\) term. If \(N\) is even only half of the last term must be counted to preclude double counting. Using equation (147) this can be written:

\[
Q(v=0) = 2A\{\exp(N\lambda_N) + N\exp(4/N \sum_{r=1}^{N-1} \lambda_r (N-2)^2/N)\lambda_N\} \\
+ \sum_{q_1=1}^{N} \sum_{q_2=1}^{N} \exp(4/N \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos((2\pi/N)r(q_i-q_j))\lambda_r) \\
\text{(q_1 < q_2)} \\
\cdot \exp((N-4)^2/N \lambda_N) + \cdots \\
+ \sum_{q_1=1}^{N} \cdots \sum_{q_N=1}^{N} \exp(4/N \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos((2\pi/N)r(q_i-q_j))\lambda_r) \\
\text{(q_1 < q_2 < \cdots < q_N)} \\
\cdot \exp((N-2n)^2/N \lambda_N) + \cdots 
\]

The exponent can be simplified by using equation (119):

\[
\frac{4}{N} \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos(2\pi/N r(q_i-q_j))\lambda_r \\
= \frac{4}{N} \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos(2\pi/N r(q_i-q_j)) \left( \sum_{s=1}^{N} \cos(2\pi/N rs)\theta_s \right) \\
= \frac{4}{N} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{s=1}^{N} \theta_s \left( \sum_{r=1}^{N} \cos(2\pi/N rs)\cos(2\pi/N r(q_i-q_j)) - 1 \right) \\
= \frac{4}{N} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{s=1}^{N} \theta_s \left( N/2(\delta_{s,q_i-q_j} + \delta_{s,q_j-q_i}) - 4n^2/N \sum_{s=1}^{N} \theta_s \right) 
\]
\[ \begin{align*}
&= 2 \sum_{i=1}^{n} \sum_{j=1}^{n} \left[ \theta(q_i - q_j)^{+} \theta_{N - (q_i - q_j)}^{+} \right]^{-4n^2/N} \lambda_N \\
&= 4 \sum_{i=1}^{n} \sum_{j=1}^{n} \theta(q_i - q_j)^{+}^{-4n^2/N} \lambda_N
\end{align*} \]

since \( \sum_{s=1}^{N} \theta = \lambda_N \), and \( \theta_{-k} = \theta_{N-k} = \theta_k \). Use was made of the following identity:

\[ \sum_{r=1}^{N} \cos(2\pi/N) kr \cos(2\pi/N) \xi r = 1/4 \sum_{r=1}^{N} (\omega_{kr} + \omega_{-kr}) \]

\[ \cdot (\omega_{kr} + \omega_{-kr}) = 1/4 \sum_{r=1}^{N} \left[ (\omega r(k+\ell) + \omega r(k-\ell) + \omega_{r(k-\ell)} + \omega_{r(k+\ell)}) \right] \]

\[ = N/2(\delta_{k,\ell} + \delta_{k,-\ell}) \]

The entire exponent is then:

\[ \frac{4}{N} \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos(2\pi/N) r(q_i - q_j) \lambda_r^{+} + (N-2n)^{2}/N \lambda_N \]

\[ = 4 \sum_{i=1}^{n} \sum_{j=1}^{n} \theta(q_i - q_j)^{+} + (N-4n)\lambda_N \]

Making this substitution in equation (150) we obtain:

\[ Q(v=0) = 2A \left\{ \exp(N\lambda_N)^{+} \right\}_{q_1=1}^{N} \exp\left\{ (N-4)\lambda_N \right\} \]

\[ + \sum_{q_1=1}^{N} \sum_{q_2=1}^{N} \exp\left\{ 4 \sum_{i=1}^{n} \sum_{j=1}^{n} \theta(q_i - q_j)^{+} + (N-8)\lambda_N \right\} \]

\( (q_1 < q_2) \)

\[ + \cdots + \sum_{q_1=1}^{N} \sum_{q_n=1}^{N} \exp\left\{ 4 \sum_{i=1}^{n} \sum_{j=1}^{n} \theta(q_i - q_j)^{+} + (N-2n)\lambda_N \right\} + \cdots \]

\( (q_1 < q_2 < \cdots < q_n) \)
where the fact that $\theta_0 = \theta_N = 0$ was used in writing the term corresponding to $n=1$. Factoring out the common term $\exp\{N\lambda_N\}$, we have finally:

$$Q(v=0) = 2A\exp\{N\theta\} \left\{ 1 + \exp\{-4\theta\} \right\}$$

$$+ 1/2! \exp\{-8\theta\} \sum_{q_1=1}^N \sum_{q_2=1}^N \exp\{4 \sum_{i=1}^2 \sum_{j=1}^2 \theta(q_i - q_j)\}$$

$$+ \ldots + 1/n! \exp\{-4n\theta\} \sum_{q_1=1}^N \ldots \sum_{q_n=1}^N \exp\{4 \sum_{i=1}^n \sum_{j=1}^n \theta(q_i - q_j)\}$$

$$+ \ldots$$

since $\lambda_N = \sum_{r=1}^N \theta_r = 0$ (see equation (36)).

In the last equation the primed summations indicate that no index may be repeated in any one term. Otherwise the summations in that equation are now unrestricted. Hence each term must be divided by $n!$ since this is its degeneracy.

If we make the following definitions:

$$x_k = \exp\{8\theta_k\} \quad (156)$$

$$\Lambda = \exp\{\lambda_N\} = \exp\{\theta\} \quad (157)$$

the partition function for $v=0$ can be written in its final form:

$$Q(v=0) = 2AA^N \sum_{n=0}^{[N/2]} T_n$$

$$= 2A' \sum_{n=0}^{[N/2]} T_n \quad (158)$$
\[ T_0 = 1 \]

\[ T_n = \Lambda^{-n} \frac{n!}{n!} \sum_{q_1=1}^{n-1} \cdots \sum_{q_n=1}^{n} \prod_{r=1}^{n} \prod_{s=1}^{n} (q_r - q_s)(1 - 1/2\delta_{n,N/2}) \] (159)

\[ A' = \begin{cases} 
\exp(Nv) & \text{(fluid)} \\
\Lambda^N = \exp(N\Theta) & \text{(ferromagnet)} 
\end{cases} \] (160)

c. The General Case, \( v \neq 0 \):

In extending the result of the previous section to the case \( v \neq 0 \) we start once more from equation (111)

\[ Q = A\text{Tr}\{\exp\left(\sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \Theta + v \sum_{r=1}^{N} Z_r\right)\} \] (111)

and consider the form:

\[ \bar{U} = \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \Theta + v \sum_{r=1}^{N} Z_r \] (161)

\[ = Y^\dagger \Phi Y + \Phi_0 \]

where

\[ Y = \zeta - \zeta_0 \] (162)
and \( \Phi \) is defined by equation (114), while \( \Phi_0 \) is a constant vector yet to be determined. \( \Phi_0 \) is likewise a constant which will be evaluated presently. Expanding the form in (161) we have:

\[
\overline{U} = \zeta^\dagger \Phi \zeta - \zeta^\dagger \Phi \zeta_0 - \zeta_0^\dagger \Phi \zeta + \zeta_0^\dagger \Phi \zeta + \Phi_0
\]

where equation (113) was used. We make therefore the following identification:

\[
\zeta^\dagger \Phi \zeta_0 + \zeta_0^\dagger \Phi \zeta = -\nu \sum_{r=1}^{N} Z_r
\]

\[
\Phi_0 = -\zeta_0^\dagger \Phi \zeta_0
\]

Observe now that:

\[
\overline{V}_N^\dagger \zeta = \zeta^\dagger \overline{V}_N = \frac{1}{\sqrt{N}} \sum_{r=1}^{N} Z_r
\]

\( \overline{V}_N \) being defined by equation (123), i.e.

\[
\overline{V}_N = \frac{1}{\sqrt{N}} \mid 1, 1, \ldots, 1 \rangle
\]

Hence we choose \( \zeta_0 = a \overline{V}_N \), where \( a \) is a constant yet to be determined, and obtain:
\[
\zeta^+ \phi \zeta_0 + \zeta_0^+ \phi \zeta = a(\zeta^+_N \lambda_N^+ \lambda_N^+ \zeta_0^*)
\]

\[
= 2a\lambda_N/\sqrt{N} \sum_{r=1}^{N} Z_r
\]

or

\[
(a + \sqrt{N} \nu / 2\lambda_N) \sum_{r=1}^{N} Z_r = 0
\]

This being an operator equation, and \( \sum_{r=1}^{N} Z_r \neq 0 \) in general, we have:

\[
a = -\sqrt{N} \nu / 2\lambda_N = -\sqrt{N} \nu / (2 \sum_{r=1}^{N} \theta_r) = -\sqrt{N} \nu / 2\theta
\]

\[
\zeta_0 = aV_N = -\nu / 2\lambda_N \mid 1, 1, \cdots, 1 \rangle
\]

\[
\phi_0 = -\zeta_0^+ \phi \zeta_0 = -a^2 V_N^+ \phi V_N = -a^2 \lambda_N^+ \lambda_N^+ V_N
\]

\[
= -a^2 \lambda_N = -N\nu^2 / 4\lambda_N^*.
\]

The partition function, equation (111), can then be written:

\[
Q = A \exp\{-a^2 \lambda_N^* \} \text{Tr}\{\exp\{Y^+ \phi Y\}\}
\]

\[
= A' \text{Tr}\{\exp\{Y^+ \phi Y\}\}
\]

The problem of diagonalizing the operator \( Y^+ \phi Y \) is now the same as that examined in the last section. We let

\[
Y = (\zeta - \zeta_0) = S_n
\]
where $S$ is defined in (124). Then

\[ Y \phi Y = \sum_{r=1}^{N} |\eta_r|^2 \lambda_r \]

and the partition function can be written:

\[ Q = A' \text{Tr} \{ \exp \left( \sum_{r=1}^{N} |\eta_r|^2 \lambda_r \right) \} \]

In a manner quite analogous to equation (132) we define $\chi_r$ by the following equation:

\[ \eta_r \psi_\alpha = \chi_r^\alpha \psi_\alpha \]  \hfill (172a)

so that $\chi_r$ is the eigenvalue of the operator $\eta_r$, and we can then write:

\[ Q = A' \sum_{\alpha=1}^{2^N} \psi_\alpha^\dagger \exp \left( \sum_{r=1}^{N} |\chi_r^\alpha|^2 \lambda_r \right) \psi_\alpha \]  \hfill (170c)

the latter sum being again a sum over macroscopic configurations. Before being able to proceed with the evaluation of this sum, it is necessary to determine $|\chi_r^\alpha(C)|^2$, since equation (147) no longer holds due to the re-definition of $\eta_r$ and hence of $\chi_r$. Furthermore, it will be necessary to re-check the consistency condition, equations (134) and (135). From equation (171), which defines $\eta$, we have:
\[ n = S^{-1}(\zeta - \zeta_0) = S^\dagger(\zeta - \zeta_0) = S^\dagger\zeta - aS^\dagger v_N \]

\[
\begin{pmatrix}
0 \\
0 \\
\vdots \\
0 \\
1
\end{pmatrix}
= S^\dagger\zeta - a
\]

where the orthonormality of the eigenvectors \( V_k \) was used. Thus:

\[
\eta_r = 1/\sqrt{N} \sum_{s=1}^{N} \exp\{-i(2\pi/N)r(s-1)\} z_s^{-a\delta} r, N \tag{173}
\]

\[
= 1/\sqrt{N} \sum_{s=1}^{N} \omega^{-r(s-1)} z_s^{-a\delta} r, N
\]

It is now possible to evaluate the eigenvalue in equation (172):

\[
\eta_r \psi_\alpha = [1/\sqrt{N} \sum_{s=1}^{N} \omega^{-r(s-1)} z_s^{-a\delta} r, N] \psi_\alpha \tag{172b}
\]

\[
= [1/\sqrt{N} \sum_{s=1}^{N} \omega^{-r(s-1)} \sigma_\alpha^{-a\delta} r, N] \psi_\alpha
\]

\[
= \chi_r^{\alpha} \psi_\alpha
\]

so that:

\[
\chi_r^{\alpha} = 1/\sqrt{N} \sum_{s=1}^{N} \omega^{-r(s-1)} \sigma_\alpha^{-a\delta} r, N
\]

We find then that for \( r \neq N \), the evaluation of \( |\chi_r| \) is identical to the case \( v=0 \); i.e.
\[ |x_r(n)|^2 = \frac{4}{N} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos\left[\frac{2\pi}{N} r(q_i - q_j)\right] \]

For \( r=N \) we have:

\[ x_N(n) = \frac{1}{\sqrt{N}} \sum_{s=1}^{N} \sigma_s = \frac{1}{\sqrt{N}} (\sigma_N - \sigma) \]

so that:

\[ |x_N(n)|^2 = \left(\frac{N+a\sqrt{N}-2n}{N}\right)^2/\frac{1}{N} \]

In summary, then:

\[ |x_r(n)|^2 = \begin{cases} \frac{4}{N} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos\left[\frac{2\pi}{N} r(q_i - q_j)\right], & (r \neq N) \\ \left(\frac{N+a\sqrt{N}-2n}{N}\right)^2/\frac{1}{N}, & (r=N) \end{cases} \]

(174)

The new consistency condition can be obtained as follows:

\[ \chi = S^\dagger(\psi-aV_N) \]

where

\[ \chi = |\chi_1, \chi_2, \ldots, \chi_N> \]

\[ \psi = |\sigma_1, \sigma_2, \ldots, \sigma_N> \]

i.e. we have rewritten equation (172) in vector form consistent with the earlier definitions of \( \psi \) and \( S \) (cf. equations (77) and (124)).
Then:

\[ x^+ x = (\psi^+ - aV_N^+)(S^+ S)(\psi - aV_N) \]  

\[ = \psi^+ \psi - a(V_N^+ \psi + \psi^+ V_N) + a^2 V_N^+ V_N \]

\[ = N - 4an/\sqrt{N} + 2a\sqrt{N}a^2 \]

This is the new consistency condition. In terms of the previous geometric picture, there has now occurred first a shift of the origin by the vector \(-aV_N\), followed by a rotation of the \(N\)-dimensional coordinate system. Consequently, the distance from the origin to the various corners of the "cube" has now changed. The distance to all corners is no longer the same but depends on \(n\), i.e. the total number of + or - signs in the corner coordinates.

The consistency condition is satisfied by every term in the expansion of (170c):

\[ \sum_{r=1}^{N} |x_r(n)|^2 = 4/N \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos[2\pi/N (r(q_i - q_j))] + (N + a\sqrt{N} - 2n)^2/N \]  

\[ = 4 \sum_{i=1}^{n} \sum_{j=1}^{n} \delta_{ij} - 4n^2/N + N + a^2 - 4n - 4an/\sqrt{N} \]

\[ = N - 4an/\sqrt{N} + 2a\sqrt{N}a^2 \]

Using these results we can write the partition function by summing macroscopic configurations corresponding to total occupancy of the system:
\[ Q = A' \sum_{r=1}^{N} g(r) \exp\{ \sum_{r=1}^{N} |x_r(C)|^2 \lambda_r \} \]

\[ = A' \left\{ g(0) \exp\{ \sum_{r=1}^{N} |x_r(0)|^2 \lambda_r \} + g(N) \exp\{ \sum_{r=1}^{N} |x_r(N)|^2 \lambda_r \} \right. \]

\[ + g(1) \exp\{ \sum_{r=1}^{N} |x_r(1)|^2 \lambda_r \} + g(N-1) \exp\{ \sum_{r=1}^{N} |x_r(N-1)|^2 \lambda_r \} \]

\[ + \cdots + g(n) \exp\{ \sum_{r=1}^{N} |x_r(n)|^2 \lambda_r \} + g(N-n) \exp\{ \sum_{r=1}^{N} |x_r(N-n)|^2 \lambda_r \} \]

\[ + \cdots \}

\[ = A' \left\{ \exp\{ N+2a/\sqrt{N}+a^2 \} \lambda_N \right\} + \exp\{ N-2a/\sqrt{N}+a^2 \} \lambda_N \}

\[ + N \left\{ \exp\{ 4/N \sum_{r=1}^{N-1} \lambda_r + (N+a^2+4/N-2a/\sqrt{N}-4+a/\sqrt{N}) \lambda_N \} \right. \]

\[ + \exp\{ 4/N \sum_{r=1}^{N-1} \lambda_r + (N+a^2+4/N-2a/\sqrt{N}+4+a/\sqrt{N}) \lambda_N \} \}

\[ + \cdots \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \exp\{ 4/N \sum_{r=1}^{N-1} \sum_{i=1}^{n} \sum_{j=1}^{n} \cos[2\pi/N \sum_{r=1}^{N-1} r(q_i-q_j)] \lambda_r \} \]

\[ (q_1<q_2<\cdots<q_n) \]

\[ \cdot \left\{ \exp\{ N+a^2+4n^2/N+2a/\sqrt{N}-4n-4an/\sqrt{N} \} \lambda_N \right\} \]

\[ + \exp\{ N+a^2+4n^2/N-2a/\sqrt{N}+4an/\sqrt{N} \} \lambda_N \}\}

\[ + \cdots \]
Using equation (152) once more this can be rewritten as follows:

\[ Q = 2A' \exp\left\{ (N+a^2)\lambda_N \right\} \left[ \cosh(2a\sqrt{N}\lambda_N) + N \cosh[2a/\sqrt{N}\lambda_N(N-2)] \exp\{-4\lambda_N\} \right. \]

\[ + \cdots + \cosh[2a/\sqrt{N}\lambda_N(N-2n)] \exp\{-4n\lambda_N\} \] (177b)

\[ \cdot \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \exp\{4 \sum_{i=1}^{n} \sum_{j=1}^{n} \theta(q_i - q_j)\} \cdots \]

\[ (q_1 < q_2 < \cdots < q_n) \]

Using the definition of \( A \), equation (169), and that of \( \lambda_N \), equation (119), together with equation (68) this can be recast in the form:

\[ Q = 2A \exp\{N\theta\} \left\{ \cosh(N\nu) + \sum_{q_1=1}^{N} \cosh[(N-2\nu)] \exp\{-4\theta\} \right. \] (177c)

\[ + \cdots + 1/n! \cosh[(N-2n)\nu] \exp\{-4n\theta\} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \exp\{4 \sum_{i=1}^{n} \sum_{j=1}^{n} \theta(q_i - q_j)\} \]

\[ + \cdots \]

where the primed but otherwise unrestricted summation of equation (155) has been introduced once more. Also the definition of \( A' \), equation (170a), was used to eliminate the \( a^2\lambda_N \) term in the exponent of the common factor.

If we introduce the definitions of equations (156) and (157) the partition function for \( \nu \neq 0 \) takes the form:

\[ Q = 2A \sum_{n=0}^{[N/2]} T_n \] (178)

\[ T_n = \cosh[(N-2n)\nu]A^{-n}t_n(1-1/2\delta_n,N/2) \]
\[ t_0 = 1 \]

\[
 t_n = 1/n! \sum_{q_1=1}^{N_1} \cdots \sum_{q_n=1}^{N_n} \prod_{r=1}^{n} \prod_{s=1}^{n} x(q_r - q_s) 
\]

\[ (r<s) \]

\[
 A = \begin{cases} 
\exp(Nv) & \text{fluid} \\
\Lambda^N = \exp(N\Theta) & \text{ferromagnet} 
\end{cases}
\]

This, then, is the desired expansion of the partition function valid, in the case of a fluid, for all ranges of \( v \), i.e. for all ranges of the chemical potential and hence all ranges of the density. In the case of the ferromagnet the solution is valid for all possible ranges of an external magnetic field.

It is straightforward, although algebraically tedious, to compute the partition function for finite \( N \) and check the result against computations by other methods which have been tabulated in Appendix I. The agreement in all cases is perfect. A typical example is the result for \( N=9 \), which will serve at the same time to illustrate the structure of the partition function.

\[
 Q_9 = 2\exp(9v)\{\cosh(9v) + 9\cosh(7v)\exp(-4\Theta) \\
+9\cosh(5v)\exp(-8\Theta)\{\exp(8\Theta_1) + \exp(8\Theta_2) + \exp(8\Theta_3) + \exp(8\Theta_4)\} \\
+9\cosh(3v)\exp(-12\Theta)\{\exp(8(2\Theta_1 + \Theta_2)) + 2\exp(8(\Theta_1 + \Theta_2 + \Theta_3)) \\
+2\exp(8(\Theta_1 + \Theta_3 + \Theta_4)) + \exp(8(2\Theta_2 + \Theta_4)) + \exp(8(\Theta_1 + 2\Theta_4)) \\
+2\exp(8(\Theta_2 + \Theta_3 + \Theta_4)) + 1/3\exp(24\Theta_3)\} \tag{179}
\]
Upon letting $\nu = 0$ and rearrangement this will be found to agree with the results in Appendix I.

The convergence and analyticity of the series solution, equation (178) will be examined in the next chapter. The proof given there shows that the quantity of interest, the grand potential $\Omega$ defined by

$$\Omega = \lim_{N \to \infty} \frac{1}{N} \ln Q = \beta p V$$

is well defined and that the limit exists. Furthermore, the series

$$\lim_{N \to \infty} Q^{1/N}$$

is absolutely convergent.

It will be observed that in summing equation (170c) in terms of macroscopic configurations corresponding to total occupancy of the system we have in fact carried out the sum by taking account of successive deviations from the perfectly ordered state. Thus, the first term in (178) corresponds to having all cells occupied or empty (all spins up or down); the next term reflects states with one cell occupied or empty (one spin deviating from the perfectly ordered state); etc. Consequently, if we wish to approximate
the solution of the problem by considering the first terms only of the series in equation (178), we find that this constitutes in fact a low-temperature approximation. This will be seen explicitly in connection with the nearest-neighbor two and three dimensional series approximations developed in Chapter VI.
CHAPTER V

CONVERGENCE AND ANALYTICITY

A. Convergence

We examine in this section the convergence of the series solution developed in the last chapter:

\[
Q = 2A T(\nu, \theta) = 2A \sum_{n=0}^{[N/2]} T_n
\]

\[
T_n = \cosh[(N-2n)\nu] \exp\{-4n\theta\} t_n (1-1/2\delta_n, N/2)
\]

\[
t_0 = 1
\]

\[
t_n = 1/n! \sum_{q_1=1}^{N'} \cdots \sum_{q_n=1}^{N'} \exp\{4 \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s) \}
\]

Let us consider initially the case \( \nu = 0 \). We are then concerned with the convergence of

\[
T(0, \theta) = \sum_{n=0}^{[N/2]} T_n = \sum_{n=0}^{[N/2]} 1/n! \exp\{-4n\theta\} \sum_{q_1=1}^{N'} \cdots \sum_{q_n=1}^{N'} \exp\{4 \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s) \}
\]

\[
(1-1/2\delta_n, N/2)
\]

We shall not restrict consideration here to a Lennard-Jones type potential but permit any attractive potential with a hard core, i.e. any potential such that \( \phi_r < 0; (r \neq 0) \) (see equation (6)). Then we have by equation (36) that

\[
\theta_r = -1/4 \beta \phi_r \geq 0
\]
since $\beta \geq 0$. Consider the exponent in (181):

$$
4 \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s)^{-4n \beta} = 4 \left[ \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s)^{-n} \sum_{r=1}^{n} \theta r \right]^{(183a)}
$$

$$
= 8 \left[ \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s)^{-n} \sum_{r=1}^{n} \theta (1-1/2 \delta_{r,N/2}) \right]^{(r>s)}
$$

We wish to determine the sign of this expression. This depends clearly on how many times a given $\theta$ occurs in the first (positive) set of terms. Of course, we are interested in this only as $N \rightarrow \infty$, since for any finite system $T$ is just a finite polynomial and thus obviously converges. However, as $N \rightarrow \infty$, symmetries due to boundary conditions disappear, and likewise the difference between $N$ even and $N$ odd becomes trivial. In that case it is apparent that the greatest multiplicity of $\theta$'s in the positive set of terms is obtained for a setting of the indices $q_i$ in (178) such that the difference between $q_i$'s is constant. As a typical example, consider a setting of the indices such that $q_1 = 1$, $q_2 = 2$, $q_3 = 3$, ..., $q_n = n$. Then $\theta_1$ occurs $(n-1)$ times, $\theta_2$ occurs $(n-2)$ times, $\theta_3$ occurs $(n-3)$ times, ..., $\theta_{n-1}$ occurs once. One readily verifies that this yields the correct number of $\theta$'s in the sum, i.e.:

$$(n-1)+(n-2)+\cdots+2+1 = \frac{1}{2} n(n-1) = \left[\frac{n}{2}\right].$$

In the particular case considered $\theta_1$ occurs most frequently in the positive terms. The total number of $\theta_1$'s in the exponent is $8[(n-1)-n]=-8$. Thus, using equation (182), we conclude that in this case the exponent is negative. A similar conclusion holds for other choices of the $q_i$'s; the highest multiplicity (barring symmetries due to the ring boundary conditions) is always
obtained for a constant setting between q's. Depending on how this constant is chosen, different θ's are singled out, but none occur with a frequency greater than (n-1). The conclusion then holds in general for an infinite system that the exponent (183) is negative. For finite systems, the matter is slightly different and somewhat more complicated, since we are then faced with symmetries introduced by the boundary conditions, and we must distinguish between N even and N odd, as was done in equation (183). One finds in that case that the highest possible multiplicity is not (n-1) but n. However, as stated this circumstance, while it will not alter the conclusion that follows, is of no consequence in determining the convergence of T.

We conclude then that:

\[
4\left[ \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s)^{-n} \sum_{r=1}^{N} \theta r \right] \leq 0
\]  

(183b)

One may verify the above results and conclusions readily by checking the partition function for N=9, equation (179). It is also possible to check the conclusion in a more general case. Suppose that all potentials are equal, i.e. that the range parameter γ defined in connection with equation (2) goes to zero. Then:

\[\epsilon = \theta_1 = \theta_2 = \cdots = \theta_{N-1}; \quad \theta_0 = \theta_N = 0; \quad \epsilon \geq 0.\]

Equation (183) becomes in that case:

\[
4\left[ \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s)^{-n} \sum_{r=1}^{N} \theta r \right] = 4[2^{\left(\frac{n}{2}\right)} - n(N-1)]\epsilon
\]

\[= 4n(n-N)\epsilon \leq 0\]
since \( n \leq N/2 \).

Noting also that all the terms in \( T \) are positive, we find that

\[
0 \leq T(0,0) = \frac{\lfloor N/2 \rfloor}{n!} \prod_{n=0}^{N/2} \left\{ \exp\left(-n \Theta \right) \sum_{q_1=1}^{N} \cdots \sum_{q_{n-1}=1}^{N} \exp\left(4 \sum_{r=1}^{n} \sum_{s=1}^{n} (q_r - q_s) \right) \right\} \cdot (1 - 1/2\delta_{n, N/2})
\]

\[
\leq \frac{\lfloor N/2 \rfloor}{n!} \prod_{n=0}^{N/2} \left\{ \exp\left(-n \Theta \right) \sum_{q_1=1}^{N} \cdots \sum_{q_{n-1}=1}^{N} \cdot (1 - 1/2\delta_{n, N/2}) \right\}
\]

\[
= \frac{\lfloor N/2 \rfloor}{n!} \prod_{n=0}^{N/2} \left\{ \frac{N}{n} \cdot (1 - 1/2\delta_{n, N/2}) \right\}
\]

\[
= \frac{1}{2} \sum_{n=0}^{N/2} \left\{ \frac{N}{n} \right\} = 2^{N-1}
\]  

(185)

In arriving at this result one may either carry out the primed summations explicitly noting that one of the \( q \)'s, say \( q_1 \), can be summed over the full range, \( q_2 \) has then a range of only \( (N-1) \), etc. Or one may simply use the fact, remarked on in the last chapter, that the degeneracy of the state corresponding to \( n \) occupied cells or \( (N-n) \) vacant cells is \( \frac{N}{n} \). We have then the following result:

\[
0 \leq Q(0,0) \leq 2^N A = \left\{ \begin{array}{ll} 2^N & \text{fluid} \\ (2\exp\{\Theta\})^N & \text{ferromagnet} \end{array} \right. 
\]  

(186)

Hence

\[
0 \leq \lim_{N \to \infty} Q(v=0)^{1/N} \leq 2^A A^{1/N} = \left\{ \begin{array}{ll} 2 & \text{fluid} \\ 2A & \text{ferromagnet} \end{array} \right. 
\]  

(187)
Thus we conclude that for \( v=0 \), \( Q^{1/N} \) converges absolutely, and hence so does the grand potential \( q \) (cf. equation (180)).

If \( v \neq 0 \), we have:

\[
0 \leq T(v,0) = \sum_{n=0}^{[N/2]} \frac{1}{n!} \cosh[(N-2n)v] \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \exp\left\{4\left[ \sum_{r=1}^{n} \sum_{s=1}^{n} \theta_{(q_r-q_s)} \right] - n\theta\right\}(1-1/2\delta_{N,N/2})
\]

\[
\leq \sum_{n=0}^{[N/2]} \binom{N}{n} \cosh[(N-2n)v](1-1/2\delta_{N,N/2})
\]

\[
= 1/2 \sum_{n=0}^{[N/2]} \binom{N}{n} \left\{ \exp\{(N-2n)v\} + \exp\{- (N-2n)v\} \right\}(1-1/2\delta_{N,N/2})
\]

\[
= 1/2 \exp(Nv) \sum_{n=0}^{[N/2]} \binom{N}{n} \left\{ \exp\{-2nv\} + \exp\{-2(N-n)v\} \right\}(1-1/2\delta_{N,N/2})
\]

\[
= 1/2 \exp(Nv) \sum_{n=0}^{N} \binom{N}{n} \exp\{-2nv\} = 1/2 \exp(Nv)(1+\exp(-2v))^N
\]

\[
= 1/2(\exp(v)+\exp(-v))^N = 2^{N-1}\cosh^N v
\]  

(188)

Consequently,

\[
0 \leq Q(v,0) \leq 2^N \cosh^N v = \begin{cases} 
(1+\exp(2v))^N & \text{(fluid)} \\
(2\cosh v)^N & \text{(ferromagnet)}
\end{cases}
\]

(189)

And hence:

\[
0 \leq \lim_{N \to \infty} Q(v,0)^{1/N} \leq 2^A 1/N \cosh v = \begin{cases} 
(1+\exp(2v))^N & \text{(fluid)} \\
2\cosh v & \text{(ferromagnet)}
\end{cases}
\]

(190)
The series solution, equation (178), consequently has the following properties under the conditions stated: 6, 22

(1) \( \lim_{N \to \infty} Q^{1/N} \) exists.

(2) \( q = \lim_{N \to \infty} 1/N \ln(Q) \) exists

(3) The series representing these functions is absolutely and uniformly convergent for all finite values of the Gibbs potential (external magnetic field).

The conclusions hold for any attractive potential with a hard repulsive core. Antiferromagnets and other systems with interaction potentials greater than zero have not been considered here, since they have no direct counterpart in the fluid case.
B. Analyticity

Let us consider once more the function $T$ appearing in (178):

$$T(v, \theta) = \sum_{n=0}^{[N/2]} T_n = \sum_{n=0}^{[N/2]} a_n(\theta) \cosh[(N-2n)v]$$

(191a)

where:

$$a_n(\theta) = \frac{1}{n!} \exp\{-4n\theta\} \prod_{q_1=1}^{N} \cdots \prod_{q_n=1}^{N} \exp\{4 \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s)\}(1-1/2\delta)_{n,N/2}$$

$$= \exp\{-4n\theta\} \prod_{q_1=1}^{N} \cdots \prod_{q_n=1}^{N} \exp\{4 \sum_{r=1}^{n} \sum_{s=1}^{n} \theta (q_r - q_s)\}(1-1/2\delta)_{n,N/2}$$

$$\quad(q_1 < q_2 < \cdots < q_n)$$

(191b)

The property of these coefficients that will be required in discussing the analyticity of the partition function are the following:

$$a_n = a_n^*$$

(192a)

$$a_n \geq 0$$

(192b)

$$a_n \leq \binom{N}{n}$$

(192c)

$$a_0 = 1$$

(192d)

$$a_n = a_{N-n}$$

(192e)

The first two properties follow directly from the fact that the potentials are real. The third property was proved in the preceding section, while the last two follow from the construction of the partition function in the last chapter (cf. equations (133), (148), and the analysis following the latter equation).
By virtue of property (192e) it is possible to rewrite \( T \) in the following form:

\[
T(v, \Theta) = \sum_{n=0}^{[N/2]} a_n \cosh[(N-2n)v] 
\]

\[
= \frac{1}{2} \sum_{n=0}^{[N/2]} a_n \left\{ \exp{(N-2n)v} + \exp{-(N-2n)v} \right\} 
\]

\[
= \frac{1}{2} y^{-N/2} \sum_{n=0}^{N} a'_n y^n \quad (a' = a_n / (1 - \delta_n, N/2)) 
\]

\[
= \frac{1}{2} y^{-N/2} P_N(\Theta, y) 
\]

where

\[
y = \exp{2v} 
\]

\[
P_N \text{ is thus an } N\text{th degree polynomial in } y. \text{ Alternatively one can write } T \text{ as follows:} 
\]

\[
T(v, \Theta) = \frac{1}{2} \exp{Nv} \sum_{n=0}^{N} a_n \exp{-2nv} 
\]

\[
= \frac{1}{2} y^{N/2} P_N(\Theta, y^{-1}) 
\]

By virtue of equations (178) and (181), we see that

\[
Q = \begin{cases} 
  P_N(\Theta, y) & \text{(fluid)} \\
  \exp{N\Theta}T(\Theta, y) & \text{(ferromagnet)} 
\end{cases} 
\]
Thus in the fluid case the partition function is analytic throughout the entire finite complex $y$ plane, but has a pole of order $N$ at the ideal point at infinity. Specifically, the point $y=0$ is a point where $Q_N$ is analytic and where $\lim_{y \to 0} Q_N$ exists, i.e. $Q_N(y=0)=1$. This is in keeping with the expected behavior of a fluid system. As we shall see later the point $y=0$, which corresponds to a negatively infinite chemical potential, represents a system of zero density, i.e. a system with no particles. By equation (180) one has then:

$$q(y=0) = \lim_{N \to \infty} \frac{1}{N} \ln Q_N = 8pV = 0$$

which implies, for nonzero temperature and volume, that the pressure is zero. Conversely the point $y=\infty$ corresponds to a positively infinite chemical potential and represents a system with every cell occupied, i.e. with a density of one. Hence one would expect the pressure for such a system to be infinite.

The partition function for the ferromagnet, on the other hand, is analytic everywhere in the complex $y$ plane except at the origin and at the ideal point at infinity. It is not analytic at these points but has poles there of order $N/2$. In order not to deal with fractional poles it is preferable to examine the behavior of the function in a complex $w$ plane related to the $y$ plane by the transformation

$$w^2 = y$$

In that plane the ferromagnetic partition function has two poles of order $N$. This is also in keeping with the expected behavior of such a system, for the point $y=0$ corresponds to a negatively infinite external
field and the point \( y = \infty \) to a positively infinite one. Since the direction of the coordinate axes is arbitrary, one would expect the behavior of the system to be the same at both points. In the ferromagnetic case the partition function is a macrocanonical one; hence one finds that the Helmholtz free energy per spin is given by: \(^{1,2}\)

\[
F = -\frac{1}{\beta} \lim_{N \to \infty} \frac{1}{N} \ln Q
\]

One finds, then, that the free energy diverges at these two points.

We wish now to examine the zeros of the partition function in the complex \( y \) (or \( w \) ) plane. While the partition function is analytic at these points, they are of interest, since \( \ln Q \) diverges there and thus is not analytic. Consequently, if we define "pressure", in the case of the fluid, as \( (1/\beta VN) \ln Q \) we can say that the "pressure" diverges at these points. While this makes no physical sense when we are dealing with complex or negative real values of \( y \), it becomes meaningful when such zeros occur on the positive real \( y \) axis, as pointed out by Yang and Lee. \(^5\) One can then associate such points with a transition of the system from one phase to another. In a heuristic way one can think of points where the "pressure" formally goes to negative infinity as particle sinks where particles leave one phase and enter another one which represents a mathematically disjoint system.

While one can no longer speak of pressure or particle sinks when zeros occur away from the positive real axis, it may perhaps still be meaningful to think of them as representing some sort of virtual transition state.

If we write

\[
y = \exp(2\nu) = r \exp(i\phi)
\]
we have, using equations (32), (34), and (36):

\[ g = \left[ \frac{1}{\beta} \ln \left( \frac{r \lambda}{\ell} \right) + \phi \right] + i \frac{\phi}{\beta} \]

so that we can think of \( g \) as a complex "chemical potential" at these points. But

\[ g = u + pv - Ts \]

Hence, considering \( u \), \( pv \) and \( T \) as real quantities, we find that the entropy is complex there also:

\[ s = \left[ \frac{1}{T} (u + pv - \phi) + k \ln \left( \frac{\ell}{r \lambda} \right) \right] - ik \phi \]

Or, in view of the well-known relationship between entropy and probability:

\[ S \propto k \ln W \]

we can write:

\[ W \propto \left( \frac{r \lambda}{\ell} \right) \exp \left\{ -\beta (u + pv + \phi) \right\} \exp \{ i \phi \} \]

The complex probability density at such zeros away from the real axis in the \( y \)-plane is therefore in keeping with the intuitive notion regarding such points as some sort of virtual transition state, the probability density becoming real as these points close in on the real axis.

To obtain some information about the distribution of zeros of the partition function we observe, as suggested earlier, that \( y=0 \) is not a
zero (cf. equations (193) and (195)). Hence the zeros of Q are the roots of \( P_N \). Since \( P_N \) is an \( N \)th degree polynomial in \( y \), Q has exactly \( N \) roots.

By property (192a) the roots occur in complex conjugate pairs. Also, since \( y=0 \) is not a root, we find that the roots of \( P_N \) coincide with the zeros of T. Hence, from equations (193a) and (193b) we have:

\[
T = \frac{1}{2} y^{-N/2} P(y) = \frac{1}{2} y^{N/2} P(1/y) = 0
\]

which implies that if \( y_k \) is a root so is \( y_k^{-1} \). Thus the zeros of Q occur in quadruplets: if \( y_k \) is the kth zero, then \( y_k^* \), \( y_k^{-1} \), and \( y_k^{*-1} \) are also zeros. It follows at once that if \( N/4 \) is not an integer at least two of the roots must merge on the unit circle. Furthermore, if \( N \) is odd one set of zeros must lie on the unit circle and on the real axis, i.e. at \( y=\pm 1 \).

By property (192b) none of the roots can lie on the positive real axis. Hence for \( N \) odd one root must lie at \( y=-1 \). The property that for \( N \) finite no roots lie on the positive real axis has important consequences. It means that for a finite system the grand potential \( q=1/N \ln Q \) is analytic everywhere except at \( y=\infty \) and, in the case of the ferromagnet, at \( y=0 \). Hence such a system can have no phase transition. While there may be behavior suggestive of an incipient transition, no actual transition can occur as long as \( N \) is finite, i.e. as long as the volume (meaning of course length in the one-dimensional case) is finite.

It is easy to find the roots of Q in the particular case when all potentials are zero except for the hard core repulsion. This corresponds to the Tonks' fluid of hard rods. The polynomial coefficients are then

\[
a_n = \binom{N}{n}, \quad \text{and so:}
\]

\[
P_N(0,y) = \sum_{n=0}^{N} \binom{N}{n} y^n = (1+y)^N
\]
Thus $y=-1$ is an $N$-fold degenerate root. This system will be examined in more detail later.

One can obtain further information about the distribution of roots in the $x$-plane by letting $W=\exp(i\phi)$ and writing $T$ in the form:

$$T(\theta, x) = \sum_{n=0}^{[N/2]} a_n(\theta) \{\cosh[(N-2n)\ln r] \cos[(N-2n)\phi] + i\sinh[(N-2n)\ln r] \sin[(N-2n)\phi]\}$$

and

$$\text{Arg}(T) = \tan^{-1} \left( \frac{\sum_{n=0}^{[N/2]} a_n(\theta) \sinh[(N-2n)\ln r] \sin[(N-2n)\phi]}{\sum_{n=0}^{[N/2]} a_n(\theta) \cosh[(N-2n)\ln r] \cos[(N-2n)\phi]} \right) \quad (196)$$

One can then select suitable contours in the $x$-plane such as the one shown in Figure 10.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{contours.png}
\caption{Contours for Locating Zeros of $T$.}
\end{figure}
In that instance we find that

$$\Delta \text{Arg}(T) = N\pi/2 = 2\pi(Z-P)$$

where $Z$ is the number of zeros and $P$ the number of poles enclosed by the contour, using a well-known theorem of complex analysis. But $T$ is analytic inside the region $R$. Therefore $T$ has $N/4$ zeros in the first quadrant of the finite $x$-plane outside the unit circle, which implies that there are $N/4$ zeros outside the unit circle in the finite upper $y$-plane, in agreement with the previous analysis concerning the pairing of roots.

In making the above analysis care is necessary on $C_3$; one must assume there that $N$ is even so as not to pass through the zero at $w=i$ which corresponds to the one at $y=-1$ for $N$ odd. The case $N$ odd can then always be recovered by recognizing that $P_N(y)=P_{N-1}(y)(1+y)$ where $(N-1)$ is even.

Using the property that zeros of the partition function occur in inverse pairs, it would follow at once that all zeros lie on the unit circle in both the $x$ and $y$ planes if one could show that

$$|y_k| \leq 1, \quad (k=1, 2, \ldots, N)$$

where $y_k$ is the $k$th root of $P_N$. Yang and Lee in fact proved this property of the zeros for an interaction potential of the type used in this study. It follows then that all roots of $P_N$ and therefore of the partition function lie on the unit circle in the $y$-plane. As $N \to \infty$ the density of these roots will become such that one has a continuous distribution which, under suitable circumstances, i.e. when $T \leq T_c$, will close in on the positive real axis causing a nonanalyticity there in the grand potential. This occurs at $y=1$, i.e. zero chemical potential, which corresponds to a density of
one-half. This is, of course, precisely where one would expect a phase transition to occur from physical intuition as well as the behavior of actual systems.

We shall see later, in studying particular systems, how the zeros distribute themselves on the unit circle and how they approach the real axis under various conditions.
Chapter VI

NEAREST-NEIGHBOR APPROXIMATIONS

In this chapter an approximation to the true intermolecular potential will be examined and applied to one, two, and three dimensional systems. The approximation is as follows:

\[ V_r = \begin{cases} 
-\zeta & (r \in \{I'\}) \\
0 & (r \notin \{I'\})
\end{cases} \]  \hspace{1cm} (197a)

or in the case of the ferromagnet

\[ J_r = \begin{cases} 
-J & (r \in \{I'\}) \\
0 & (r \notin \{I'\})
\end{cases} \]  \hspace{1cm} (197b)

where \( \{I'\} \) is a prescribed set of integers. In addition, we shall retain the hard-core repulsion which has been built into the model, but shall assume formally as before that \( V_0 = V_N = J_0 = J_N = 0 \). This approximation is usually referred to as the nearest-neighbor approximation \(^5,11,12\), since only bonds between nearest-neighbor particles are nonzero, while all other interactions are considered to vanish. While perhaps not realistic physically, the approximation is not a bad one if one considers that the strength of the interaction between next-nearest neighbors is only \( 1\% \) of the nearest-neighbor interaction if the Lennard-Jones potential with \( \gamma = 6 \) (cf. equation (2)) is used.

This approximation has the advantage of permitting complete evaluation of the partition function in the one-dimensional case which allows comparison with the closed-form solution attainable by matrix methods, thus
establishing the validity of the present solution. In the two and three dimensional case the approximation allows expansion of the partition function in a low-temperature series by a convenient algebraic method. Again, comparison with expansions obtained in other ways shows excellent agreement.
A. One-Dimensional System

In the case of the one-dimensional fluid the potential in equation (197) becomes:

\[ V_r = \begin{cases} 
-\zeta & (r=1) \\
0 & (r\neq1) 
\end{cases} \tag{197} \]

The ferromagnetic case will not be treated separately since it parallels identically the fluid case. We have then from equations (6), (36), and (156) that:

\[ X_r = \exp\{4(\delta_{r,1} + \delta_{r,N-1})\varepsilon\} \tag{198a} \]

\[ = \exp\{4\varepsilon\Delta_{r,1}\} \]

where

\[ \epsilon = 2\theta_1 = 2\theta_{N-1} = \frac{1}{4} \beta\zeta = -\frac{1}{2} \beta\phi_1 = -\frac{1}{2} \beta\phi_{N-1} \]

\[ \Delta_{r,s} = \delta_{r,s} + \delta_{r,N-s} \quad \text{(mod. N)} \]

(cf. equations (6) and (36)). It is more convenient to use the following form of \( X_r \), which follows from (198) either by inspection or series expansion of the exponential:

\[ X_r = 1 + a\Delta_{r,1} \tag{198b} \]

\[ a = (x_1 - 1) \quad ; \quad x_i = \exp\{4\varepsilon\} = \exp\{\beta\varepsilon\} \]

The partition function, equation (178), is then:

\[ Q = 2A \sum_{n=0}^{[N/2]} \frac{2^n}{n!} \cosh[(N-2n)v] \exp\{-4n\epsilon\} t_n(1 - \frac{1}{2} \delta_{n,N/2}) \tag{178} \]

\[ t_n = \frac{1}{n!} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \prod_{r=1}^{n} \prod_{s=1}^{n} (1 + a\Delta_{q_r-q_s}, 1) \tag{199} \]

\[ = \frac{1}{n!} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \prod_{r=1}^{n} \prod_{s=1}^{n} (1 + a\Delta_{q_r-q_s}, 1)(1 - \delta_{q_r, q_s}) \]
The last $\delta$-function factor has been introduced here to eliminate the primed summations. Before proceeding with the evaluation of equation (199), it is desirable to expand the primed sums in terms of unprimed summations not involving $\delta$-functions. Noting that the functions to be summed (i.e. $X(q_r - q_s)$ in general and $1 + a \Delta q_r - q_s$ in this instance) are symmetric in the indices $q_r$ and $q_s$, we wish to expand:

$$
\sum_{q_1}^{N'} \cdots \sum_{q_n}^{N'} f(q_1, q_2, \ldots, q_n) = \sum_{q_1}^{N} \cdots \sum_{q_n}^{N} \prod_{q_r=1}^{n} \prod_{q_s=1}^{n} f(q_r, q_s) \\
(1 - \delta_{q_r, q_s})
$$

(200a)

where

$$f(q_r, q_s) = f(q_s, q_r)$$

We shall use for convenience the abbreviated notation

$$\sum_{q_1=1}^{N'} \cdots \sum_{q_n=1}^{N'} \equiv \sum_{q_1 \cdots q_n=1}^{N}$$

and shall designate a contracted index as follows:

$$\sum_{q_1 q_2 q_3 \cdots q_i \cdots q_j \cdots q_n}^{N} = \sum_{q_1=1}^{N} \sum_{q_2=1}^{N} \cdots \sum_{q_i=1}^{N} \sum_{q_j=1}^{N} \sum_{q_n=1}^{N}$$

$$= \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \delta_{q_i, q_j}$$

For $n=1$ the primed sum is trivial, yielding just $N$. For $n=2$ we have:

$$\sum_{q_1 q_2} \left(1 - \delta_{q_1, q_2}\right) f(q_1, q_2) = \left(\sum_{q_1} q_2 - \sum_{q_1} \sum_{q_2}\right) f(q_1, q_2)$$

$$= \sum_{q_1} q_2 f(q_1, q_2) - N$$

(200b)
And for $n=3$:

$$
\sum_{q_1 q_2 q_3} \prod_{r=1}^{3} \prod_{s=1}^{3} (1 - \delta_{q_r, q_s}) f(q_r, q_s)
$$

(200c)

$$
= \{ \sum_{q_1 q_2 q_3} - 3 \sum_{q_1 q_2 q_3} + 3 \sum_{q_1 q_2 q_3} - \sum_{q_1 q_2 q_3} \}
\cdot f(q_1, q_2) f(q_1, q_3) f(q_2, q_3)
$$

$$
= \{ \sum_{q_1 q_2 q_3} - 3 \sum_{q_1 q_2 q_3} + 2 \sum_{q_1 q_2 q_3} \} f(q_1, q_2) \cdots f(q_2, q_3)
$$

$$
= \sum_{q_1 q_2 q_3} f(q_1, q_2) \cdots f(q_2, q_3) - 3 \sum_{q_1 q_2} f(q_1, q_2)^2 + 2N
$$

where the dummy nature of the indices was used, i.e. contraction of any two indices is equivalent. For $n=4$ a direct expansion of the $\delta$-function products yields the correct sums, although the tedious algebra can be avoided by arguments analogous to those used below in the case $n=5$. One obtains in either way:

$$
\sum_{q_1 q_2 q_3 q_4} \prod_{r=1}^{4} \prod_{s=1}^{4} (1 - \delta_{q_r, q_s}) f(q_r, q_s)
$$

(200d)

$$
= \{ \sum_{q_1 q_2 q_3 q_4} - 6 \sum_{q_1 q_2 q_3 q_4} + 8 \sum_{q_1 q_2 q_3 q_4} + 3 \sum_{q_1 q_2 q_3 q_4} \}
\cdot \prod_{r=1}^{4} \prod_{s=1}^{4} f(q_r, q_s)
$$

$$
= \sum_{q_1 q_2 q_3 q_4} \prod_{r=1}^{4} \prod_{s=1}^{4} f(q_r, q_s) - 6 \sum_{q_1 q_2 q_3} f(q_1, q_2)^2 f(q_1, q_3)^2
$$

$$
\cdot f(q_2, q_3) + \sum_{q_1 q_2} [8f(q_1, q_2)^3 + 3f(q_1, q_2)^4] - 6N
$$

Direct expansion of the $\delta$-function products is very tedious for $n=5$ and higher order terms. One can obtain the correct expansion of the primed sums much more conveniently by the following considerations.
Write \( \sum q_1 q_2 q_3 q_4 q_5 = \sum q_1 q_2 q_3 q_4 q_5 + \) correction terms. As a first correction it is necessary to subtract all coincidences of pairs of indices. There are \( \binom{5}{2} = 10 \) such coincidences, all of them equivalent. Hence corrected to first order we have \( \sum q_1 q_2 q_3 q_4 q_5 = \sum q_1 q_2 q_3 q_4 q_5 - 10 \sum q_1 q_2 q_3 q_4 q_5 + \) other terms. We note now that we have over-compensated for double coincidences; e.g. the contraction \( \sum q_1 q_2 q_3 q_4 q_5 \) has been subtracted once with the contraction \( \sum q_1 q_2 q_3 q_4 q_5 \) and once with the contraction \( \sum q_1 q_2 q_3 q_4 q_5 \). Thus \( \binom{5}{2} \binom{3}{2} = 30 \) double contractions of this type have been subtracted, whereas only 15 should have been so that we have:

\[
\sum q_1 q_2 q_3 q_4 q_5 = \sum q_1 q_2 q_3 q_4 q_5 - 10 \sum q_1 q_2 q_3 q_4 q_5 + 15 \sum q_1 q_2 q_3 q_4 q_5 + \text{other terms}
\]

Considering triple contractions next one observes that each single contraction gives rise to three triple contractions whereas we should have subtracted only \( \binom{5}{3} = 10 \). Hence

\[
\sum q_1 q_2 q_3 q_4 q_5 = \sum q_1 q_2 q_3 q_4 q_5 - 10 \sum q_1 q_2 q_3 q_4 q_5 + 15 \sum q_1 q_2 q_3 q_4 q_5 + 20 \sum q_1 q_2 q_3 q_4 q_5 + \cdots
\]

Contractions like \( \sum q_1 q_2 q_3 q_4 q_5 \) have also been overcompensated for. There should have been \( \binom{5}{2} \binom{3}{2} = 10 \) of these subtracted. Instead we subtracted 40 (each single contraction gives rise to four double-triple contractions, e.g. \( \sum q_1 q_2 q_3 q_4 q_5 + \sum q_1 q_2 q_3 q_4 q_5 \) and \( \sum q_1 q_2 q_3 q_4 q_5 \) and \( \sum q_1 q_2 q_3 q_4 q_5 \)). Further, the double contractions each allow two ways of forming a double-triple contraction, while each triple contraction allows one double-triple contraction. There has been a net addition of 10 such contractions; to compensate for this we must write:
Furthermore, there should have been \( \binom{5}{4} = 5 \) quadruple contractions.

Actually we have added 25 of these and must now subtract 30 of them.

Finally as regards total contractions 25 were subtracted whereas one should have been. We have then, altogether, the following expansion:

\[
\sum' \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} f(q_r, q_s) = \left( \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} f(q_r, q_s) \right) - 10 \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} f(q_r, q_s)
\]

\[
+ 15 \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} f(q_r, q_s) + 20 \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} f(q_r, q_s)
\]

\[
- 30 \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} f(q_r, q_s) + 24 \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} f(q_r, q_s)
\]

As a quick check on the expansions, equations (200a) through (200e) one may observe that when the interaction potentials go to zero, \( f(q_r, q_s) = 1 \) for all values of the indices \( q_r \) and \( q_s \). In that case the sums reduce to \( N!/(N-n)! \) \( n=1,2,3,4,5 \) as they should, so that \( t_n = \binom{N}{n} \).

It is now possible to determine explicitly the terms in the partition function, equation (199). Clearly:
\[ t_0 = 1 \]  
\[ t_1 = \sum_{q_1} 1 = N \]  
\[ t_2 = (1/2) \{ \sum_{q_1} q_2 (1 + a\Delta_{q_1-q_2,1}) - N \} \]  
\[ = (1/2) \{ N^2 + 2aN - N \} = (N/2) [N+2X_1-3] \]  
\[ t_3 = (1/3!) \{ \sum_{q_1} q_2 q_3 (1+a\Delta_{q_1-q_2,1})(1+a\Delta_{q_1-q_3,1})(1+a\Delta_{q_2-q_3,1}) \} \]  
\[ - 3 \sum_{q_1} q_2 (1+a\Delta_{q_1-q_2,1})^2 + 2N \]  
\[ \text{Now,} \]  
\[ \sum_{q_1} q_2 q_3 (1+a\Delta_{q_1-q_2,1})(1+a\Delta_{q_1-q_3,1})(1+a\Delta_{q_2-q_3,1}) \]  
\[ = \sum_{q_1} q_2 q_3 \{1 + 3a\Delta_{q_1-q_2,1} + 3a^2\Delta_{q_1-q_2,1} \Delta_{q_1-q_3,1} + a^3\Delta_{q_1-q_2,1} \} = N^3 + 6aN^2 + 12a^2N + 0 \]  
\[ = N[N^2 + 6(N-4)X_1 + 12X_1^2 + 6(2-N)] \]  
where the following result was used:  
\[ \sum_{q_1} q_2 q_3 \Delta_{q_1-q_2,1} \Delta_{q_1-q_3,1} \Delta_{q_2-q_3,1} \]  
\[ = \sum_{q_1} q_2 [\delta_{q_1,q_2+1} \delta_{q_1,q_2} + \delta_{q_1,q_2+1} \delta_{q_1,q_2+2} + \delta_{q_1,q_2+1} \delta_{q_2,q_1+2} + \delta_{q_1,q_2+1} \delta_{q_2,q_1+1} \delta_{q_1,q_2+2} + \delta_{q_2,q_1+1} \delta_{q_1,q_2+2} + \delta_{q_2,q_1+2} \delta_{q_1,q_2+1}] = 0 \]  
since all \( \delta \)-function products in this sum are incompatible. This sum will be needed again later in determining higher order terms. The following will also be needed:  
\[ \sum_{q_1} q_2 (1 + a\Delta_{q_1-q_2,1})^2 = \sum_{q_1} q_2 \{1+2a\Delta_{q_1-q_2,1} + a^2(\Delta_{q_1-q_2,1})^2 \} \]  
\[ = \sum_{q_1} q_2 \{1+(2a+a^2)\Delta_{q_1-q_2,1} \} \]  
\[ = N^2 + 2N(X_1^2-1) \]
Combining these results we have:

\[ t_3 = \frac{N}{3!} [6x_1^2 + 6(N-4)x_1 + (N-5)(N-4)] \]  

(201d)

The following computations are required for \( t_4 \):

\[ \sum_q \delta_{(q_1,q_2)} \delta_{(q_1,q_3)} \delta_{(q_1,q_4)} \delta_{(q_1,q_5)} = \sum_q \sum_r \sum_s \sum_t \delta_{(q_1,q_2)} \delta_{(q_1,q_3)} \delta_{(q_1,q_4)} \delta_{(q_1,q_5)} = 2 \sum_q \sum_r \sum_s \sum_t \delta_{(q_1,q_2)} \delta_{(q_1,q_3)} \delta_{(q_1,q_4)} \delta_{(q_1,q_5)} = 8N \]  

(203)

\[ \sum_q \sum_r \sum_s \sum_t \delta_{(q_1,q_2)} \delta_{(q_1,q_3)} \delta_{(q_1,q_4)} \delta_{(q_1,q_5)} = 2 \sum_q \sum_r \sum_s \sum_t \delta_{(q_1,q_2)} \delta_{(q_1,q_3)} \delta_{(q_1,q_4)} \delta_{(q_1,q_5)} = 0 \]  

(204)

\[ \sum_q \sum_r \sum_s \sum_t \delta_{(q_1,q_2)} \delta_{(q_1,q_3)} \delta_{(q_1,q_4)} \delta_{(q_1,q_5)} = 6N \]  

(205)

Equation (202) was used in connection with equation (204). One can also arrive at this result by a topological argument which will be useful later. It is apparent from the construction of the \( \delta \)-functions (cf. equations (198a) and (198b)) that they are associated with the Boltzmann factors representing nonvanishing interactions, i.e. nearest-neighbor interactions. We can therefore think of \( \delta_{(q_1,q_2)} \) as representing a bond between cells \( q_r \) and \( q_s \). From that point of view equation (202) can be interpreted as saying that any triangle of bonds makes a vanishing contribution to the partition function. Equation (204) broadens this result by stating that any open four-sided figure of bonds which includes a triangle also makes a vanishing contribution. Figure 11 illustrates this, as well as some of the other configurations required in the evaluation of \( t_3 \) and \( t_4 \). Thus we have (cf. equation (200)): 
Non-Vanishing Contributions

Vanishing Contributions

Figure 11. Typical Bond Configurations for $t_3$ and $t_4$.

\[
t_4 = \frac{1}{4!} \sum_{q_1, q_2, q_3, q_4} \prod_{r=1}^{4} \prod_{s=1}^{4} (1 + a \Delta (q_r - q_s), 1) - 6 \sum_{q_1, q_2, q_3} (r < s)
\]

\[
= \sum_{q_1, q_2, q_3} (1 + a \Delta (q_1 - q_2), 1)^2 (1 + a \Delta (q_1 - q_3), 1)^2 (1 + a \Delta (q_2 - q_3), 1) + 3 (1 + a \Delta (q_1 - q_2), 1)^4 - 6N
\]

Now,

\[
\sum_{q_1, q_2} (1 + a \Delta (q_1 - q_2), 1)^3 = \sum_{q_1, q_2} [1 + (3a + 3a^2 + a^3) \Delta (q_1 - q_2), 1]
\]

\[
= \sum_{q_1, q_2} [1 + (X_1^3 - 1) \Delta (q_1 - q_2), 1] = N[N + 2(X_1^3 - 1)]
\]

Similarly:

\[
\sum_{q_1, q_2} (1 + a \Delta (q_1 - q_2), 1)^4 = \sum_{q_1, q_2} [1 + (X_1^4 - 1) \Delta (q_1 - q_2), 1]
\]

\[
= N[N + 2(X_1^4 - 1)]
\]
\[ \sum q_1 q_2 q_3 (1 + a \Delta (q_1 - q_2), 1)^2 (1 + a \Delta (q_1 - q_3), 1)^2 (1 + a \Delta (q_2 - q_3), 1)^2 \]  

= \[ \sum q_1 q_2 q_3 \left[ 1 + (2a + a^2) \Delta (q_1 - q_2), 1 \right] \left[ 1 + (2a + a^2) \Delta (q_1 - q_3), 1 \right] \]  

\cdot \left[ 1 + a \Delta (q_2 - q_3), 1 \right] = \sum q_1 q_2 q_3 \left[ 1 + (2x_1^2 + x_1 - 3) \Delta (q_1 - q_2), 1 \right]  

+ (x_1^4 + 2x_1^3 - 4x_1^2 - 2x_1 + 3) \Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1  

+ (x_1^2 - 1)(x_1 - 1) \Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1 \Delta (q_2 - q_3), 1 \]  

= N \left[ N^2 + 2N(2x_1^2 + x_1 - 3) + 4(x_1^4 + 2x_1^3 - 4x_1^2 - 2x_1 + 3) \right]  

\[ \sum q_1 q_2 q_3 q_4 (1 + a \Delta (q_1 - q_2), 1)(1 + a \Delta (q_1 - q_3), 1) \cdots (1 + a \Delta (q_3 - q_4), 1) \]  

= \[ \sum q_1 q_2 q_3 q_4 \left\{ 1 + 6a \Delta (q_1 - q_2), 1 + 15a^2 \Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1 \right\} \]  

\cdot \left[ 1 + 6a^3 \Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1 \Delta (q_1 - q_4), 1 \right]  

+ 16a^3 \Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1 \Delta (q_1 - q_4), 1  

\cdot \left[ x_1 - 1 \right] \Delta (q_1 - q_3), 1 \Delta (q_2 - q_3), 1 + 12a^4 \Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1 \]  

\[ \Delta (q_1 - q_4), 1 \Delta (q_3 - q_4), 1 \]  

+ 3a^4 \left[ \Delta (q_1 - q_2), 1 \Delta (q_2 - q_3), 1 \Delta (q_3 - q_4), 1 \Delta (q_1 - q_4), 1 \right] \]  

\[ + 6a^5 \Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1 \Delta (q_1 - q_4), 1 \Delta (q_2 - q_3), 1 \Delta (q_2 - q_4), 1 \]  

\[ + a^5 \Delta (q_1 - q_2), 1 \cdots \Delta (q_3 - q_4), 1 \right\} = N^3 \left[ N^2 + 12(x_1 - 1)N^2 \right] \]  

+ 60(x_1^2 - 2x_1 + 1)N + 18x_1^4 + 56x_1^3 - 276x_1^2 + 312x_1 - 108 \]  

Considerations leading to equation (209) were as follows: There are \( \binom{6}{3} = 20 \) ways of distributing three bonds among a four-cell system; of
these four are triangular and hence vanishing configurations leaving
16 nonvanishing contributions like Figure 11(1) or variations thereof
while 12 configurations include triangles and thus vanish (cf.
Fig. 11 (4). All combinations of five and six bonds among four
cells include triangles and therefore vanish.

In this way we obtain:

\[ t_4 = \frac{N}{4!} \left[ 24X_1^3 + 36(N-5)X_1^2 + 12(N-6)(N-5)X_1 + (N-7)(N-6)(N-5) \right] \]  

(201e)

The next term in the partition function expansion is:

\[ t_5 = \frac{1}{5!} \left\{ \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} (1 + a \Delta(q_r - q_s), 1)^2 \right\} \]

\[ \cdot (1 + a \Delta(q_1 - q_2), 1)^2 (1 + a \Delta(q_1 - q_3), 1)^2 (1 + a \Delta(q_1 - q_4), 1)^2 \]

\[ \cdot (1 + a \Delta(q_2 - q_3), 1)(1 + a \Delta(q_2 - q_4), 1)(1 + a \Delta(q_2 - q_5), 1) \]

\[ + 15 \sum q_1 q_2 q_3 (1 + a \Delta(q_1 - q_2), 1)^4 (1 + a \Delta(q_1 - q_3), 1)^2 (1 + a \Delta(q_2 - q_3), 1)^2 \]

\[ + 20 \sum q_1 q_2 q_3 (1 + a \Delta(q_1 - q_2), 1)^3 (1 + a \Delta(q_1 - q_3), 1)^3 (1 + a \Delta(q_2 - q_3), 1) \]

\[ - 20 \sum q_1 q_2 (1 + a \Delta(q_1 - q_2), 1)^4 - 30 \sum q_1 q_2 (1 + a \Delta(q_1 - q_2), 1)^4 + 24N \]  

(201f)

The following results will be needed to evaluate this term:

\[ \sum_{k=1}^{m} \binom{m}{k} a^k = \sum_{k=1}^{m} \binom{m}{k} (X_1 - 1)^k = \sum_{k=1}^{m} \sum_{\ell=0}^{k} \binom{m}{k} \binom{k}{\ell} (-1)^{k-\ell} X_1^\ell \]

(210)

\[ = \sum_{\ell=1}^{m} X_1^\ell \sum_{k=\ell}^{m} \binom{m}{k} \binom{k}{\ell} (-1)^{k-\ell} + \sum_{k=1}^{m} \binom{m}{k} (-1)^{k} \]

\[ = \sum_{\ell=1}^{m} X_1^\ell \sum_{r=0}^{\ell} \binom{m}{\ell+r} \binom{\ell+r}{r} (-1)^r - 1 = \sum_{\ell=1}^{m} \sum_{r=0}^{\ell} \binom{m}{r} \delta_{m, \ell+r} - 1 = X_1^m - 1 \]
where use was made of the following
\[
\sum_{k=0}^{m} \binom{m}{k} (-1)^k = 0 \tag{211}
\]
and
\[
\binom{r-s}{t} = (-1)^t \binom{s-r+t-1}{t} \tag{212}
\]
which follows directly from the definitions of the factorial symbol and providing we further define
\[
\binom{a}{b} = \frac{1}{b!} (a)(a-1)\cdots(a-b+1) \quad \text{if } a < 0.
\]

Also, the following computations will be required:
\[
\sum q_1 q_2 (1+aA(q_1-q_2),1)^4 = N[N+2(X_1^4-1)] \tag{213}
\]
\[
\sum q_1 q_2 (1+aA(q_1-q_2),1)^6 = N[N+2(X_1^6-1)] \tag{214}
\]
\[
\sum q_1 q_2 q_3 (1+aA(q_1-q_2),1)^3 (1+aA(q_1-q_3),1)^3 (1+aA(q_2-q_3),1)^3
\]
\[
= \sum q_1 q_2 q_3 [1+(2X_1^3+X_1^{-3})A(q_1-q_2),1] + (X_1^3-1)^2A(q_1-q_2),1
\]
\[
\cdot A(q_1-q_3),1 + 2(X_1^3-1)(X_1^{-1})A(q_1-q_2),1 \Delta(q_2-q_3),1
\]
\[
+ \text{zero terms} = N[N^2 + 2N(2X_1^3 + X_1^{-3})
\]
\[
+ 4(X_1^6 + 2X_1^4 - 4X_1^2 - 2X_1 + 3)]
\]
\[
\sum q_1 q_2 q_3 (1+aA(q_1-q_2),1)^n (1+aA(q_1-q_3),1)^2 (1+aA(q_2-q_3),1)^2
\]
\[
= N[N^2 + 2N(X_1^4 + 2X_1^2 - 3) + 4(2X_1^6 - X_1^4 - 4X_1^2 + 3)]
\]
\[
\sum_{q_1 q_2 q_3 q_4} \left(1 + a^\Delta (q_1 - q_2), 1 \right)^2 \left(1 + a^\Delta (q_1 - q_3), 1 \right)^2 \left(1 + a^\Delta (q_1 - q_4), 1 \right)^2 (1 + a^\Delta (q_2 - q_3), 1) (1 + a^\Delta (q_2 - q_4), 1) (1 + a^\Delta (q_3 - q_4), 1)
\]
\[= N^3 + 2N^2 (5X^2_1 + 5X^2_1 - 6) + 4X(5X^4_1 + 9X^3_1 - 12X^2_1 - 15X^1_1 + 15)
\]
\[+ 2(13X^6_1 + 6X^5_1 - 9X^4_1 - 84X^3_1 + 51X^2_1 + 71X^1_1 - 55)]
\]
\[
\sum_{q_1 q_2 q_3 q_4 q_5} \prod_{s=1}^{5} \prod_{r<s}^5 (1 + a^\Delta (q_r - q_s), 1) = \sum_{q_1 q_2 q_3 q_4 q_5} (1 + 10a^\Delta (q_1 - q_2), 1)
\]
\[+ 45a^2\Delta (q_1 - q_2), 1 \Delta (q_1 - q_3), 1 + 110a^3\Delta (q_1 - q_2), 1
\]
\[\cdot \Delta (q_1 - q_3), 1 \Delta (q_1 - q_4), 1 + 15a^4\Delta (q_1 - q_2), 1 \Delta (q_1 - q_4), 1
\]
\[\cdot \Delta (q_2 - q_3), 1 \Delta (q_3 - q_4), 1 + 125a^4\Delta (q_1 - q_2), 1 \Delta (q_2 - q_3), 1
\]
\[\cdot \Delta (q_3 - q_4), 1 \Delta (q_4 - q_5), 1 + 60a^5\Delta (q_1 - q_2), 1 \Delta (q_1 - q_4), 1
\]
\[\cdot \Delta (q_1 - q_5), 1 \Delta (q_2 - q_3), 1 \Delta (q_3 - q_4), 1 + 10a^6\Delta (q_1 - q_2), 1
\]
\[\cdot \Delta (q_1 - q_4), 1 \Delta (q_1 - q_5), 1 \Delta (q_2 - q_3), 1 \Delta (q_3 - q_4), 1 \Delta (q_3 - q_5), 1
\]
\[+ \text{zero terms} = N^4 + 20N^3(X^1_1 - 1) + 180N^2(X^2_1 - 2X^1_1 + 1)
\]
\[+ 10N(9X^4_1 + 52X^3_1 - 210X^2_1 + 228X^1_1 - 79) + 20(5X^6_1 + 6X^5_1
\]
\[+ 5X^4_1 - 140X^3_1 + 315X^2_1 - 250X^1_1 + 69)]
\]

The arguments used in arriving at equation (217) are comparable to those discussed following equation (209) and will therefore not be repeated. In connection with equation (218) the considerations were as follows:
The sum includes $\binom{10}{1}=10$ equivalent single bonds, each yielding $2N^4$.

There are $\binom{10}{2}=45$ equivalent sets of two bonds, each of which yields $4N^3$.

Altogether there are $\binom{10}{3}=120$ triple bonds. Of these 10 are triangles, which vanish in the sum, since there are $\binom{5}{3}=10$ ways of arranging such a figure on a lattice of 5 cells (cf. Fig. 12(a)(1)). There are then 110 non-vanishing equivalent triple bonds each yielding $8N^2$.

Nonvanishing quadruple bonds consist of either a closed quadrilateral and variations thereof or of an open configuration of four bonds (cf. Fig. 12(b)(2), (3), and (4)). Of the former there are three equivalent forms.

(a) Typical Vanishing Configurations

(b) Typical Non-Vanishing Configurations

Figure 12. Typical Bond Configurations for $t_5$. 
For each there are five ways of arranging the free corner. Hence altogether one has 15 such nonvanishing quadrilaterals, each contributing $6N^2$. The number of open type four-bond configurations equivalent to Fig.12(b)(4) is most readily determined by observing that there are $\binom{10}{4}=210$ quadruple bond configurations; 15 of these have been accounted for. Vanishing quadruple bond configurations are those involving triangles like Fig.12(a)(2) and (3). Of the former there are 60 altogether, since the open corner can be arranged in five ways, and for any given open corner there are $\binom{4}{3}=4$ ways of arranging the triangle; once the triangle has been fixed the open side can be attached in three ways. Of the second type there are $\binom{5}{2}=10$. Hence the sum includes $(210-15-60-10)=125$ equivalent open quadruple-bond configurations, each of which has the value $2^4N=16N$.

Most of the quintuple bond configurations involve triangles and thus vanish by a straightforward extension of equation (204). The pentagon configuration is zero also, as a simple computation shows; after carrying out the sums involved one has incompatible $\delta$-functions as in the triangle case. Nonvanishing quintuple bond configurations are of the type shown in Fig.12(b)(5). For each such configuration one can attach the free bond in four ways. There are three topologically equivalent configurations of the closed quadrilateral. Finally, the open side can be chosen in five ways. Thus there are altogether $4\times3\times5=60$ non-zero quintuplet bond configurations. By a straightforward extension of equation (205), each of these yields $2\cdot6N=12N$.

Sextuplet bond configurations are nearly all zero except for the type shown in Fig.12(b)(6) and its topologically equivalent
variants. The number of these non-zero configurations may be determined by observing that in all of them two subscripts are repeated three times, while the others are repeated twice. Or, topologically, two corners each have three bonds entering, while all others have two bonds each. Thus the total number of such configurations is \( \binom{5}{2}\binom{3}{3} = 10 \). All these configurations are equivalent, each contributing:

\[
\sum_{q_1q_2q_3q_4q_5} \Delta(q_1-q_2), l \Delta(q_1-q_4), l \Delta(q_1-q_5), l \Delta(q_2-q_3), l \Delta(q_3-q_4), l
\]

\[
\cdot \Delta(q_3-q_4), l \Delta(q_3-q_5), l
\]

\[
= \sum_{q_1q_2q_3q_4} \Delta(q_1-q_2), l \Delta(q_1-q_4), l \Delta(q_2-q_3), l \Delta(q_3-q_4), l
\]

\[
\cdot (2\delta_{q_1,q_3} + \delta_{q_1,q_3+2} + \delta_{q_1,q_3-2})
\]

\[
= \sum_{q_1q_2q_3} \Delta(q_1-q_2), l \Delta(q_2-q_3), l (2\delta_{q_1,q_2} + \delta_{q_1,q_3+2} + \delta_{q_1,q_3-2})^2
\]

\[
= \sum_{q_1q_3} (2\delta_{q_1,q_3} + \delta_{q_1,q_3+2} + \delta_{q_1,q_3-2})^3
\]

\[
= \sum_{q_1q_3} (8\delta_{q_1,q_3} + \delta_{q_1,q_3+2} + \delta_{q_1,q_3-2}) = 10N
\]

Finally, all configurations with more than six bonds contain either triangles or pentagons and consequently do not contribute to the sum.

One obtains then for the entire term:

\[
t_5 = \frac{N}{5!} [120X_1^4 + 240(N-6)X_1^3 + 120(N-7)(N-6)X_1^2 + 20(N-8)(N-7)
\]

\[
\cdot (N-6)X_1 + (N-9)(N-8)(N-7)(N-6)]
\]

(201f)
The nearest-neighbor partition function correct to this term is:

\[ Q = 2A \cosh(N\nu) + N X^{-1} \cosh[(N-2)\nu] + \frac{N^2}{2} X^{-2}(2X_1 + N-3) \cosh [(N-4)\nu] \]

\[ + \frac{N}{3!} X^{-3} \left[ 6X_1^2 + 6(N-4)X_1 + (N-5)(N-4) \right] \cosh[(N-6)\nu] \]

\[ + \frac{N}{4!} X^{-4} \left[ 24X_1^3 + 36(N-5)X_1^2 + 12(N-6)(N-5)X_1 + (N-7)(N-6)(N-5) \right] \cosh[(N-8)\nu] \]

\[ + \frac{N}{5!} X^{-5} \left[ 120X_1^4 + 240(N-6)X_1^3 + 120(N-7) \right] \cosh[(N-10)\nu] + \ldots \]

\[ \text{(220)} \]

Examination of the partition function in equation (220) suggests strongly that one should be able to write the one-dimensional nearest-neighbor solution in the following form:

\[ Q = 2 \sum_{n=0}^{[N/2]} T_n \]

\[ \text{(221a)} \]

\[ T_n = \frac{N}{n!} \cosh[(N-2n)\nu] \sum_{k=1}^{n} \binom{n}{k}(N-n-1)X_1^{-k} \left( 1 - \frac{1}{2} \delta_{n,N/2} \right) \]

\[ \text{(n\neq0)} \]

\[ T_0 = \cosh(N\nu) \]

\[ t_n = \frac{N}{n!} \sum_{k=1}^{n} \binom{n}{k}(N-n-1)X_1^{-n-k} \]

\[ \text{(221c)} \]

While explicit proof of this conclusion does not appear feasible, the following numerical analysis leaves little doubt that the partition function in equation (221) is in fact correct. To this end, the computer program at Appendix IIIIA, written in PL 1 language, computes the coefficients of \( a = (X_1 - 1) \) directly from equation (199):
\[ t_n = \frac{1}{n!} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \prod_{r=1}^{n} \prod_{s=1}^{n} (1+\alpha \Delta (q_r-q_s), 1) \prod_{r<s}^{(r<s)} \]  
(199)

\[ \sum_{r=0}^{\infty} C_r a^r \]

As Appendix IIIA shows, coefficients \( C_r \) were computed for systems ranging from \( N=10 \) to \( N=20 \) and for various \( n \)'s.

The second program written in a form of FORTRAN IV, and exhibited in Appendix IIIB computes the same coefficients from equation (221c) in the following form:

\[ t_n = \frac{n}{n} \sum_{k=1}^{n} \binom{n}{k}(\binom{N-n-1}{k-1}) \times 1^{n-k} \left( 1 - \frac{1}{2} \delta_{n,N/2} \right) \]  
(221c)

\[ = \frac{n}{n} \sum_{k=1}^{n} \binom{n}{k}(\binom{N-n-1}{k-1})(1+\alpha)^{n-k} \left( 1 - \frac{1}{2} \delta_{n,N/2} \right) \]

\[ = \frac{n}{n} \sum_{k=1}^{n} \sum_{\ell=0}^{n-k} \binom{n}{k}(\binom{N-n-1}{k-1})(n-k)^\ell a^\ell \]

\[ = \frac{n}{n} \sum_{k=1}^{n} \sum_{\ell=0}^{n-k} \binom{n}{k}(\binom{N-n-1}{k-1})(n-k)^\ell a^\ell = \sum_{\ell=0}^{\infty} C_\ell a^\ell \]

so that

\[ C_\ell = \frac{n}{n} \sum_{k=1}^{n} \binom{n}{k}(\binom{N-n-1}{k-1})(n-k)^\ell \]  
(222)

Comparison of the results of these two programs shows that the coefficients computed by these two methods agree completely.

Coefficients were not computed for \( N>20 \), since computer time became excessive for the PL 1 program.

Computer analysis thus provides very persuasive evidence that the nearest-neighbor partition function as given by equation (221)
is correct. It is possible to rewrite the solution in (221) so that the summation indicated there can be carried out and the partition function can be exhibited in closed form. To do so it is desirable to introduce a change in the order of summation:

\[ Q = 2A \sum_{n=0}^{[N/2]} T_n = 2A\cosh(N\nu) + N \sum_{n=1}^{[N/2]} \frac{1}{k} \binom{n}{k-1} X_k^{-k} \]

\[ \cdot \cosh((N-2n)\nu)(1 - \frac{1}{2} \delta_{n,N/2}) = 2A\cosh(N\nu) + N \sum_{k=1}^{[N/2]} \frac{1}{k} X_k^{-k} \]

\[ \cdot \sum_{n=k}^{[N/2]} \binom{n-1}{k-1} \binom{N-n-1}{k-1} \cosh((N-2n)\nu)(1 - \frac{1}{2} \delta_{n,N/2}) \]  

(221d)

Consider now the case \( \nu = 0 \) first. Then we have

\[ \sum_{k=1}^{[N/2]} \frac{N}{k} X_k^{-k} \sum_{n=k}^{[N/2]} \binom{n-1}{k-1} \binom{N-n-1}{k-1} (1 - \frac{1}{2} \delta_{n,N/2}) = \sum_{k=1}^{[N/2]} \frac{N}{2k} X_k^{-k} \]

\[ \cdot \sum_{n=k}^{N-k} \binom{n-1}{k-1} \binom{N-n-1}{k-1} \]

Here the symmetry of the summand with respect to the substitution \( n+N-n \) was used in order to eliminate the \( \delta \)-function term. Using equation (212) this can be put in the form:

\[ \sum_{n=k}^{N-k} \binom{n-1}{k-1} \binom{N-n-1}{k-1} = \sum_{n=k}^{N-k} (-1)^{\alpha+\beta} \binom{n+\alpha-N}{\alpha} \binom{\beta-n}{\beta} \]  

(223)

where \( \alpha \) and \( \beta \) are parameters to be determined. We choose:

\[ \alpha = R + N-n \quad ; \quad \beta = P + n \]

so that

\[ \sum_{n=k}^{N-k} \binom{n-1}{k-1} \binom{N-n-1}{k-1} = \sum_{n=k}^{N-k} (-1)^{R+P+N} (\frac{R}{R+N-n}) (\frac{P}{P+n}) \]

\[ \cdot \frac{(R+N-n)! (P+n)! (-R-1)! (-P-1)!}{[(k-1)!]^2 (n-k)! (N-n-k)!} \]

If we now let \( R = P = -k \), this becomes:
Let \( w = n - k \), then:

\[
\sum_{n=k}^{N-k} \binom{n-1}{k-1} \binom{N-n-1}{k-1} = \sum_{n=k}^{N-k} (-1)^{N-2k} \binom{-k}{N-k-n} \binom{-k}{n-k}
\]

Here we let \( \ell = N - 2k \). Also, equation (212) was used a second time. In addition the following identity was employed:

\[
\sum_{r=0}^{k} \binom{m}{r} \binom{n}{k-r} = \binom{m+n}{k}
\]  

which is proved readily by considering the identity:

\[
(1+x)^N = \sum_{k=0}^{N} \binom{N}{k} x^k = (1+x)^m(1+x)^n = \sum_{r=0}^{m} \sum_{s=0}^{n} \binom{m}{r} \binom{n}{s} x^{r+s}
\]

Or

\[
\sum_{k=0}^{N} \left[ \binom{N}{k} - \sum_{r=0}^{k} \binom{m}{r} \binom{n}{k-r} \right] x^k = 0
\]

Recognizing now that this must hold for arbitrary \( x \) and letting \( m+n = N \), equation (224) follows.

Equation (222) then becomes, using (223):

\[
\sum_{k=1}^{[N/2]} \frac{N}{2k} x^{-k} \sum_{n=k}^{N-k} \binom{n-1}{k-1} \binom{N-n-1}{k-1} = \sum_{k=1}^{[N/2]} \frac{N}{2k} \binom{N-1}{N-2k} x^{-k}
\]

\[
= \sum_{k=1}^{[N/2]} \binom{N}{2k} x^{-k}
\]
Or:

\[ O(v=0) = 2^N \sum_{k=0}^{[N/2]} \left( \binom{N}{2k} \right) x_1^{-k} = A \sum_{k=0}^{N} \binom{N}{k} (1+(-1)^k) x_1^{-k/2} \]

\[ = A \left[ (1+x_1^{-1/2})^N + (1-x_1^{-1/2})^N \right] \]

\[ = 2^N A \exp \left(-Ne\right) \left( \cosh Ne + \sinh Ne \right) \]

For the ferromagnet \( A=\exp(Ne) \) in the nearest-neighbor case, so that

\[ O_N = 2^N \left( \cosh Ne + \sinh Ne \right) \]

Equation (226) agrees with the partition function for the one-dimensional ferromagnet with nearest-neighbor interactions and in the absence of an external magnetic field (\( v=0 \)) as developed by matrix methods in Appendix IV. The preceding expansion consequently shows the validity of the solution, equation (178), by proving that it yields the correct partition function appropriate to the present approximation.

Extension of the equivalence proof to the case when \( v \neq 0 \), i.e. when there is an external field present in the ferromagnetic case, is rather laborious. The proof is given in Appendix V and shows the complete equivalence of the one-dimensional nearest-neighbor solution obtained from equation (178) with that derived by the matrix method in Appendix IV. The equivalence proof thus establishes the validity of the solution, equation (178), at least in the nearest-neighbor approximation.

While the derivation in Appendix IV is of course much shorter and more direct, it is not applicable to the two or three dimensional case, whereas the above derivation, with minor modifications, is applicable as will be seen in the next section. The partition
function in equation (178), furthermore, is capable of dealing with the full range of intermolecular interactions, whereas the method of Appendix IV applies only to nearest-neighbor interactions in one dimension.
B. Two-Dimensional System

It is the purpose of this section to develop a series expansion for the partition function of a two dimensional system with nearest-neighbor interactions of the type discussed in Chapter IID(1). The first few terms of this series will be computed explicitly.

Let the two dimensional system under consideration have \( N \) cells with \( m \) cells per row and \( N/m \) rows (cf. Fig. 5). The potential assumed will be that given in equation (60):

\[
V_r = \begin{cases} 
  -\zeta & \text{(r=1,m)} \\
  0 & \text{(r\neq1,m)} 
\end{cases} \pmod{N} \tag{60a}
\]

\[
J_r = \begin{cases} 
  -J & \text{(r=1,m)} \\
  0 & \text{(r\neq1,m)} 
\end{cases} \pmod{N} \tag{60b}
\]

(see also equation (197)). We have then (cf. equations (198) through (200)):

\[
\epsilon = 2\theta_1 = 2\theta_m = 2\theta_{N-1} = 2\theta_{N-m} = \frac{1}{4} \beta \xi \tag{227}
\]

\[
X_r = \exp\{4\epsilon(\delta_{r,1} + \delta_{r,m} + \delta_{r,N-1} + \delta_{r,N-m})\} \tag{228}
\]

\[
= \exp\{4\epsilon \Delta_r\} = 1 + a \Delta_r
\]

where:

\[
a = X_1-1 \quad ; \quad X_1 = \exp\{4\epsilon\} \tag{229}
\]

\[
\Delta_r = \delta_{r,1} + \delta_{r,m} + \delta_{r,N-1} + \delta_{r,N-m} \pmod{N} \tag{230}
\]

The appropriate partition function is then:

\[
Q = 2A \sum_{n=0}^{[N/2]} T_n \tag{178}
\]

*The definition of the \( \Delta \)-symbol in equation (230) involves a slight change in notation from that used in equation (198). This is to avoid very cumbersome subscripting.*
\[ T_n = \cosh[(N-2n)v] X_1^{-2n} t_n(1 - \frac{1}{2} \delta_{n,N/2}) \]  
\[ t_n = \frac{1}{n!} \prod_{q_1=1}^{N'} \prod_{q_n=1}^{N'} \prod_{r=1}^{n} \prod_{s=1}^{n} (1+a\Delta(q_r-q_s))^{-1} \]  

In (231) the factor \( X_1^{-2n} \) results from the fact that:

\[ \Theta = \sum_{r=1}^{N} (\delta_{r,1} + \delta_{r,m} + \delta_{r,N-1} + \delta_{r,N-1} \theta_1 = 4\theta_1 = 2\epsilon \]

so that the term \( \exp{-4n\Theta} \) appearing in \( T_n \) becomes \( \exp{-8n\epsilon} = X_1^{-2n} \).

Using now the primed sum expansions developed in equations (199) through (200) it is possible to write down the successive terms of the partition function in a way that generally parallels the one-dimensional case except for the differences introduced by the new definitions of the \( \Delta \)-symbols. We shall assume in the expansion that follows that the system is sufficiently large (i.e. \( N \to \infty \)) so that \( m \ll N \). We find then:

\[ t_0 = 1 \]  
\[ t_1 = N \]  
\[ t_2 = \frac{1}{2} \left( \sum_{q_1} \sum_{q_2} (1+a\Delta(q_1-q_2)) - N \right) = \frac{1}{2}(N^2 + 4aN - N) \]

\[ = \frac{N}{2} [N + 4X_1 - 5] \]

since

\[ \sum_{q_1} \sum_{q_2} \Delta(q_1-q_2) = \sum_{q_1=1}^{N} \sum_{q_2=1}^{N} (\delta_{q_1-q_2,1} + \delta_{q_1-q_2,m} + \delta_{q_1-q_2,N-1} + \delta_{q_1-q_2,N-m}) = 4N \]  

(234)
In this connection it must be remembered that the $\delta$-functions are defined modulo $N$ as are the potentials which they represent.

$$t_3 = \frac{1}{3!} \left( \sum q_1 q_2 q_3 (1+a\Delta(q_1-q_2))(1+a\Delta(q_1-q_3))(1+a\Delta(q_2-q_3)) \right)$$

$$- 3\sum q_1 q_2 (1+a\Delta(q_1-q_2))^2 + 2N = \frac{1}{3!} \left( \sum q_1 q_2 q_3 (1+3a\Delta(q_1-q_2)) + 3a^2\Delta(q_1-q_2)\Delta(q_1-q_3) + a^3\Delta(q_1-q_2)\Delta(q_1-q_3)\Delta(q_2-q_3) \right)$$

$$- 3\sum q_1 q_2 \left[ 1 + (2a + a^2) \Delta(q_1-q_2) \right] + 2N}$$

$$= \frac{1}{3!} \left[ N^3 + 12aN^2 + 48a^2N - 3N^2 - 12N(2a + a^2) + 2N \right]$$

$$= \frac{N}{3!} \left[ 36X^2 + 12(N-8)X + N^2 - 15N + 62 \right]$$

The following results were used in this evaluation:

$$\sum q_1 q_2 q_3 \Delta(q_1-q_2) \Delta(q_1-q_3) = \sum q_1 q_2 \Delta(q_1-q_2) \left[ \sum q_3 \Delta(q_1-q_3) \right]$$

$$= 4\sum q_1 q_2 \Delta(q_1-q_2) = 16N$$

$$\sum q_1 q_2 q_3 \Delta(q_1-q_2) \Delta(q_1-q_3) \Delta(q_2-q_3) = 0$$

The last result follows immediately by expansion of the $\delta$-functions involved. As in the one-dimensional case, then, triangular bond configurations make a vanishing contribution.

In computing $t_4$ the following sum is required:

$$\sum q_1 q_2 q_3 q_4 \Delta(q_1-q_2) \Delta(q_2-q_3) \Delta(q_3-q_4) \Delta(q_4-q_1)$$

This corresponds to the closed quadrilateral in Fig. 11 (2). Direct evaluation of the products involved is possible but very tedious. A more convenient method is the following, where only the effect of the successive summation on the subscripts is shown:
The small numbers at the lower right of the parentheses indicate the degeneracy of each state. Thus, \( q_4 + (2m+1)_3 \) indicates a state characterized by a bond between two cells separated by \((q_4 + 2m+1)\) cell parameters, whatever the current value of \( q_4 \) may be in the sum, while the small subscript 3 indicates that there are 3 pairs of cells in this state. The last summation on \( q_3 \) is nonzero only where the states (i.e. subscripts) agree. Where they do agree, one obtains, of course, a contribution of one for each term. Thus the sum yields 36, while the remaining summation on \( q_4 \) yields \( N \). Or, altogether:

\[
\sum q_1q_2q_3q_4 \Delta(q_1-q_2) \Delta(q_2-q_3) \Delta(q_3-q_4) \Delta(q_1-q_4) = 36N \quad (237)
\]

Then:
The terms to be evaluated are:

\[ \sum_{q_1} q_2 (1 + a \Delta (q_1 - q_2))^3 = \sum_{q_1} q_2 \left[ 1 + (3a + 3a^2 + a^3) \Delta (q_1 - q_2) \right] \]

\[ = N[N + 4 (x_1^3 - 1)] \]

\[ \sum_{q_1} q_2 (1 + a \Delta (q_1 - q_2))^4 = N[N + 4(x_1^4 - 1)] \]

\[ \sum_{q_1} q_2 (1 + a \Delta (q_1 - q_2))^2 (1 + a \Delta (q_1 - q_3))^2 (1 + a \Delta (q_2 - q_3)) \]

\[ = \sum_{q_1} q_2 q_3 \left[ 1 + (2x_1^2 + x_1 - 3) \Delta (q_1 - q_2) + (x_1^4 + 2x_1^3 - 4x_1^2 - 2x_1 + 3) \right. \]

\[ \cdot \Delta (q_1 - q_2) \Delta (q_1 - q_3) + (x_1^2 - 1)(x_1 - 1) \Delta (q_1 - q_2)^2 \Delta (q_1 - q_3) \Delta (q_2 - q_3) \]

\[ = N[N^2 + 4(2x_1^2 + x_1 - 3)N + 16(x_1^4 + 2x_1^3 - 4x_1^2 - 2x_1 + 3)] \]

where equations (208) and (234) through (236) were used.

\[ \sum_{q_1} q_2 q_3 q_4 (1 + a \Delta (q_1 - q_2))(1 + a \Delta (q_1 - q_3)) \cdots (1 + a \Delta (q_3 - q_4)) \]

\[ = \sum_{q_1} q_2 q_3 q_4 [1 + 6a \Delta (q_1 - q_2) + 15a^2 \Delta (q_1 - q_2)^2 \Delta (q_1 - q_3) + 16a^3 \Delta (q_1 - q_2)^3 \]

\[ \cdot \Delta (q_1 - q_3) \Delta (q_1 - q_4) + 4a^3 \Delta (q_1 - q_2) \Delta (q_1 - q_3) \Delta (q_2 - q_3) + 12a^4 \Delta (q_1 - q_2)^2 \Delta (q_1 - q_3) \]

\[ \cdot \Delta (q_1 - q_3) \Delta (q_1 - q_4) \Delta (q_3 - q_4) + 3a^4 \Delta (q_1 - q_2) \Delta (q_1 - q_3) \Delta (q_2 - q_3) \Delta (q_3 - q_4) \]

\[ + 6a^5 \Delta (q_1 - q_2) \Delta (q_1 - q_3) \Delta (q_1 - q_4) \Delta (q_2 - q_3) \Delta (q_3 - q_4) + a^6 \Delta (q_1 - q_2) \]

\[ \cdots \Delta (q_3 - q_4) = N[N^3 + 24N^2a + 240Na^2 + 1024a^3 + 108a^4] \]

\[ = N[N^3 + 24N^2(x_1^3 - 1) + 240N(x_1^2 - 2x_1 + 1) + 108x_1^4 - 592x_1^3 - 2424x_1^2 + 2640x_1 - 916] \]
Here the expansion of equation (209) was used. While the actual sums are, of course, different the considerations leading to the various $\Delta$-factor combinations are identical to those discussed in connection with equation (209). Combining these results we have:

$$t_4 = \frac{N}{4!} [N^3 + 6N^2 (4x_1^4 - 5) + N(192x_1^2 - 504x_1 + 323) + 24(x_1^4 + 18x_1^3 - 85x_1^2 + 188x_1)
$$

$$-1254]$$

$$= \frac{N}{4!} [24x_1^4 + 432x_1^3 + 24(8N - 85)x_1^2 + 24(N^2 - 21N + 118)x_1 + N^3
$$

$$-30N^2 + 323N - 1254]$$

In evaluating $t_5$, several additional sums of $\Delta$-products are required:

$$\sum q_1 q_2 q_3 q_4 q_5 \Delta(q_1 - q_2) \Delta(q_2 - q_3) \Delta(q_3 - q_4) \Delta(q_4 - q_5) \Delta(q_1 - q_5) = 0$$

(243)

This is a pentagon configuration, which makes a vanishing contribution, just as in the one-dimensional case. Direct expansion of this $\Delta$-function product is very tedious, but an analysis like that leading to equation (237) yields the desired result very readily, particularly since the subscript display used there has mirror symmetry, so that only half need be used. This type of analysis also makes it obvious that any closed bond polygon with an odd number of sides will make a vanishing contribution.

$$\sum q_1 q_2 q_3 q_4 q_5 \Delta(q_1 - q_2) \Delta(q_1 - q_4) \Delta(q_2 - q_3) \Delta(q_2 - q_4) \Delta(q_3 - q_5)
$$

$$= \sum q_1 q_2 q_3 q_4 \Delta(q_1 - q_2) \Delta(q_1 - q_4) \Delta(q_2 - q_3) \Delta(q_3 - q_4) (4 \delta_{q_1, q_3}
$$

$$+ 2 \delta_{q_1, q_3 + m} + 2 \delta_{q_1, q_3 + m - 1} + 2 \delta_{q_1, q_3 - m} + 2 \delta_{q_1, q_3 - m - 1}
$$

$$+ \delta_{q_1, q_3 + 2m} + \delta_{q_1, q_3 + 2} \delta_{q_1, q_3 - 2} + \delta_{q_1, q_3 - 2m})$$

(244)
\[ \sum_{q_1 q_2 q_3} \Lambda(q_1 - q_2) \Lambda(q_2 - q_3) (4 \delta_{q_1, q_3} + 2 \delta_{q_1, q_3 + m + 1} + \cdots + \delta_{q_1, q_3 - 2m})^2 \]

\[ = \sum_{q_1 q_3} (4 \delta_{q_1, q_3} + 2 \delta_{q_1, q_3 + m + 1} + \cdots + \delta_{q_1, q_3 - 2m})^3 \]

\[ = \sum_{q_1 q_3} (64 \delta_{q_1, q_3} + 8 \delta_{q_1, q_3 + m + 1} + 8 \delta_{q_1, q_3 + m - 1} + 8 \delta_{q_1, q_3 - m + 1} + 8 \delta_{q_1, q_3 - m - 1} + \delta_{q_1, q_3 + 2m} + \delta_{q_1, q_3 + 2} + \delta_{q_1, q_3 - 2} + \delta_{q_1, q_3 - 2m} + \text{zero terms}) \]

\[ = 100N \]

This sum corresponds to the bond configuration in Fig. 12 (b)(6).

Then (cf. equation (201)(f)):

\[ t_5 = \frac{1}{3!} \sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} (1 + a \Lambda(q_r - q_s)) \]

\[ -10 \sum_{q_1 q_2 q_3 q_4} (1 + a \Lambda(q_1 - q_2))^2 (1 + a \Lambda(q_1 - q_3))^2 (1 + a \Lambda(q_1 - q_4))^2 \]

\[ \cdot (1 + a \Lambda(q_2 - q_3))(1 + a \Lambda(q_2 - q_4))(1 + a \Lambda(q_3 - q_4)) \]

\[ + \sum_{q_1 q_2 q_3} [15(1 + a \Lambda(q_1 - q_2))^4 (1 + a \Lambda(q_1 - q_3))^2 (1 + a \Lambda(q_2 - q_3))^2 \]

\[ + 20(1 + a \Lambda(q_1 - q_2))^3 (1 + a \Lambda(q_1 - q_3))^3 (1 + a \Lambda(q_2 - q_3))] \]

\[ = \sum_{q_1 q_2} [20(1 + a \Lambda(q_1 - q_2))^6 + 30(1 + a \Lambda(q_1 - q_2))^4] + 24N \] \hspace{1cm} (233f)

Results needed to evaluate this term are:

\[ \sum_{q_1 q_2} (1 + a \Lambda(q_1 - q_2))^4 = N[N + 4(x_1^4 - 1)] \] \hspace{1cm} (245)

\[ \sum_{q_1 q_2} (1 + a \Lambda(q_1 - q_2))^6 = N[N + 4(x_1^6 - 1)] \] \hspace{1cm} (246)
\[
\sum_{q_1 q_2 q_3} \left(1 + a \Delta (q_1 - q_2) \right)^3 \left(1 + a \Delta (q_1 - q_3) \right)^3 \left(1 + a \Delta (q_2 - q_3) \right)
\]

\[
= \sum_{q_1 q_2 q_3} \left[1 + (2x_1^3 + x_1 - 3) \Delta (q_1 - q_2) + (x_1^3 - 1) \Delta (q_1 - q_2) \Delta (q_1 - q_3) \right] \\
+ 2(x_1^3 - 1)(x_1 - 1) \Delta (q_1 - q_2) \Delta (q_2 - q_3) \right] \\
= N[N^2 + 4N(2x_1^3 + x_1 - 3) + 16(x_1^6 + 4x_1^4 - 4x_1^3 - 2x_1 + 3)]
\]  

Here equations (215), (234), (235), and (236) were used.

\[
\sum_{q_1 q_2 q_3} (1 + a \Delta (q_1 - q_2))^4 (1 + a \Delta (q_1 - q_3))^2 (1 + a \Delta (q_2 - q_3))^2 \\
= N[N^2 + 4N(x_1^4 + 2x_1^2 - 3) + 16(2x_1^6 - x_1^4 - 4x_1^2 + 3)] 
\]  

(c.f. equation (216).

\[
\sum_{q_1 q_2 q_3 q_4} (1 + a \Delta (q_1 - q_2))^2 (1 + a \Delta (q_1 - q_3))^2 (1 + a \Delta (q_1 - q_4))^2 (1 + a \Delta (q_2 - q_3)) \\
\cdot (1 + a \Delta (q_2 - q_4))(1 + a \Delta (q_3 - q_4))
\]

\[
= N[N^3 + 12N^2(x_1^2 + x_1 - 2) + 48N(x_1^4 + 3x_1^3 - 4x_1^2 - 5x_1 + 5) \\
+ 4(43x_1^6 + 42x_1^5 - 27x_1^4 - 372x_1^3 + 213x_1^2 + 330x_1 - 229)]
\]

The expansion is comparable to that leading to equation (217).

\[
\sum_{q_1 q_2 q_3 q_4 q_5} \prod_{r=1}^{5} \prod_{s=1}^{5} (1 + a \Delta (q_r - q_s)) \\
\sum_{r<s}
\]

\[
= \sum_{q_1 q_2 q_3 q_4 q_5} [1 + 10a \Delta (q_1 - q_5) + 45a^2 \Delta (q_1 - q_2) \Delta (q_1 - q_3)] \\
+ 10a^3 \Delta (q_1 - q_2) \Delta (q_1 - q_3) \Delta (q_1 - q_4) \\
+ 15a^4 \Delta (q_1 - q_2) \Delta (q_1 - q_4) \Delta (q_2 - q_3) \Delta (q_3 - q_4) \\
+ 125a^4 \Delta (q_1 - q_2) \Delta (q_2 - q_3) \Delta (q_3 - q_4) \Delta (q_4 - q_5) \\
+ 60a^5 \Delta (q_1 - q_2) \Delta (q_1 - q_4) \Delta (q_1 - q_5) \Delta (q_2 - q_3) \Delta (q_3 - q_4)
\]

\[\text{(247)}\]

\[\text{(248)}\]

\[\text{(249)}\]

\[\text{(250)}\]
\[ + 10a^6 \Delta(q_1-q_2) \Delta(q_1-q_3) \Delta(q_2-q_4) \Delta(q_3-q_5) \]

+ zero terms] 

\[ = N^5 + 40aN^4 + 720a^2N^3 + 7040a^3N^2 + 540a^4N + 3200a^5N + 8640a^6N \]

\[ = N[N^4 + 40(x_1 - 1)N^3 + 720(x_1^2 - 2x_1 + 1)N^2 + 20(27x_1^4 + 244x_1^3 - 894x_1^2) \]

\[ + 948x_1 - 325)N + 40(25x_1^6 + 66x_1^5 + 95x_1^4 - 1540x_1^3 + 3015x_1^2 - 2270x_1 + 609)] \]

The analysis leading to the expansion above is identical to that given following equation (218). In the evaluation of the \( \Delta \)-function products equations (234) through (237), (243), and (244) were used. The entire term is then:

\[ t_5 = \frac{N}{5!} \left[ N^4 + 10N^3(4x_1 - 5) + 5N^2(120x_1^2 - 312x_1 + 199) \right] \tag{233f} \]

\[ + 10N(12x_1^4 + 360x_1^3 - 1584x_1^2 + 2144x_1 - 937) \]

\[ + 120(8x_1^5 + 43x_1^4 - 400x_1^3 + 926x_1^2 - 872x_1 + 295) + 24 \]

\[ = \frac{N}{5!} \left[ 960x_1^5 + 120(N + 43)x_1^4 + 1200(3N - 40)x_1^3 + 120(5N^2 - 132N + 926)x_1^2 \right] \]

\[ + 40(N^2 - 39N^2 + 536N - 2616)x_1 + (N^4 - 50N^3 + 995N^2 - 9370N + 35424) \]

Combining these results we can write the partition function for a two-dimensional system with nearest-neighbor interactions as follows:

\[ Q = 2A[\cosh(NV) + Nx_1^2 \cosh((N-2)V)] \]

\[ + \frac{N}{2!} x_1^{-4} [N + 4x_1 - 5 \cosh((N-4)V)] \]

\[ + \frac{N}{3!} x_1^{-6} [36x_1^2 + 12(N-8)x_1 + N^2 - 15N + 62] \cosh((N-6)V) \]

\[ + \frac{N}{4!} x_1^{-8} [24x_1^4 + 432x_1^3 + 24(8N-85)x_1^2 + 24(N^2 - 21N + 118)x_1 \]

\[ + N^3 - 30N^2 + 323N - 1254] \cosh((N-8)V) \]
\[ Q = 2A \cosh(Nv) + Nx_1^{-2}\cosh[(N-2)v] \]

\[
+ \frac{N}{2!} x_1^{-4}[N + 4x_1 - 5] \cosh[(N-4)v]
\]

\[
+ \frac{N}{3!} x_1^{-6}[N^2 + 3N(4x_1 - 5) + 36x_1^2 - 96x_1 + 62] \cosh[(N-6)v]
\]

\[
+ \frac{N}{4!} x_1^{-8}[N^3 + 6N^2(4x_1 - 5) + N(192x_1^2 - 504x_1 + 323) + 24(x_1^4 + 18x_3^3\cosh[(N-8)v]
\]

\[
- 85x_1^2 + 118x_1] - 1254] \cosh[(N-8)v]
\]

\[
+ \frac{N}{5!} x_1^{-10}[N^4 + 10N^3(4x_1 - 5) + 5N^2(120x_1^2 - 312x_1 + 199)]
\]

\[
+ 10N(12x_1^4 + 360x_1^3 - 1584x_1^2 + 2144x_1 - 937)
\]

\[
+ 120(8x_1^5 + 43x_1^4 - 400x_1^3 + 926x_1^2 - 872x_1 + 35424)]
\]

\[
cosh[(N-10)v] + \ldots \}
\]

This is not the most useful form of the partition function, since the series clearly diverges as \(N \to \infty\). For determining the thermodynamic properties of the system (cf. equation (180)) a series expansion of \(Q^{1/N}\) will be of far greater utility. This will also permit comparison with the results of authors whose series are generally written in that form. In order to obtain such a series, we first expand the partition function again as a power series in \(y\) if \(v < 0\) or \(y^{-1}\) if \(v > 0\), exactly as in equation (193a) or (193b). Assuming for the moment that \(v \leq 0\), the partition function is then:
\[ Q = Ay^{-N/2} \sum_{n=0}^{N} a_n y^n \]  

(252)

where \( A \) is defined by equation (178), \( y \) by equation (194), and

\[ a_n = a_{N-n} = a_n(N,x_1) = x_1^{-2n} t_n(N,x_1) \]  

(253)

The \( t_n \)'s are, of course, given by the above expansion, i.e. equation (233). Designating:

\[ K(y,x_1) = [Q(y,x_1)]^{1/N} \]  

(254)

and assuming that \( K \) can also be expanded in a power series we wish to solve the following equation for \( K \):

\[ [K(y,x_1)]^N = [A^{1/N} y^{-1/2} (a_0 + \sum_{r=1}^{\infty} \alpha_r y^r)]^N \]  

(255)

\[ = Ay^{-N/2} \alpha_0^N \sum_{s=0}^{N} (\sum_{r=1}^{\infty} \beta_r y^r)^s \]  

\[ = Ay^{-N/2} \sum_{n=0}^{N} a_n y^n \]  

Or:

\[ \alpha_0^N \sum_{s=0}^{N} (\sum_{r=1}^{\infty} \beta_r y^r)^s = \sum_{n=0}^{N} a_n y^n \]  

(256)

\[ \alpha_0^N [1 + N(\sum r \beta_r y^r) + (\frac{N}{2})(\sum r \beta_r y^r)^2 + \ldots] \]

\[ = 1 + a_1(N,x_1)y + a_2(N,x_1)y^2 + \ldots \]

Comparing the first term we see that \( \alpha_0 = 1 \). Hence:

\[ N(\sum r \beta_r y^r) + (\frac{N}{2})(\sum r \beta_r y^r)^2 + (\frac{N}{3})(\sum r \beta_r y^r)^3 + \ldots \]  

(257)

\[ = a_1(N,x_1)y + a_2(N,x_1)y^2 + a_3(N,x_1)y^3 + \ldots \]

One can now use a very convenient technique due to Domb for evaluating the coefficients \( \beta_r \). \(^{12}\) Observe that if we let \( N=1 \) in equation (257)
all terms on the left-hand side of the equation vanish except the first, since \( \frac{1}{r} = 0 \) for \( r > 1 \). Therefore:

\[
\sum_r \beta_r y^r = a_1(1,x_1) y + a_2(1,x_1) y^2 + \ldots
\]  

(258)

so that, since \( y \) is arbitrary:

\[ \beta_r = a_r(1,x_1) \]

A more tedious procedure is the comparison of powers of \( y \) in (257). Both methods will, of course, give the same result as a quick check shows. In this way one obtains:

\[
Q^{1/N} = K(y,x_1) = A^{1/N} y^{-1/2} \left( 1 + x_1^{-2} y + 2(x_1^{-3} - x_1^{-4})y^2 + \ldots \right)
\]

\[
+ 2(3x_1^{-4} - 7x_1^{-5} + 4x_1^{-6})y^3 + (x_1^{-8} + 18x_1^{-5} - 77x_1^{-6} + 98x_1^{-7} - 40x_1^{-8})y^4
\]

\[
+ (8x_1^{-5} + 44x_1^{-6} - 370x_1^{-7} + 799x_1^{-8} - 706x_1^{-9} + 225x_1^{-10})y^5 + \ldots
\]

where

\[
A^{1/N} = \exp\{v\} = y^{1/2} \]  \hspace{1cm} \text{(fluid)}

\[
\exp\{2\varepsilon\} = x_1^{1/2} \]  \hspace{1cm} \text{(ferromagnet)}

For \( \varepsilon > 0 \) equation (260) remains unchanged except that we must replace \( y \) by \( y^{-1} \) and factor out a factor of \( y^{1/2} \) in lieu of \( y^{-1/2} \).

Comparison of the two-dimensional partition function series derived above with that given by Hill (ref. 3, equation (44.37)) and obtained by entirely different methods shows complete agreement with equation (260) above. Allowance must, of course, be made for the difference in notation*. Domb also gives an expansion of \( Q \) itself (cf. ref. 12, equation (141)) which shows perfect agreement with equation (251b) above, although Domb's expansion does not go as far as the one here.

*Hill's \( x_1 \) corresponds to \( x_1^{-1} \) in this paper.
It should be noted that the series expansion given is in terms of deviations from a perfectly ordered state. This is obvious from the derivation of the partition function, equation (178). Consequently, the series expansion derived here may be considered a low-temperature expansion of the partition function. Hill shows how a high temperature expansion may be obtained directly from the low-temperature series, at least in the two-dimensional case of a square lattice.
C. Three-Dimensional System:

The method of deriving a series expansion for the partition function of a three-dimensional system closely parallels the two-dimensional case treated in the last section. The procedure will therefore only be presented in outline form with emphasis on significant differences from the two-dimensional derivation.

We suppose, as in Chapter II D (1), that the system consists of \( N \) cells arranged in \( p \) layers with \( m \) cells per row and \( n \) rows per layer (cf. Fig. 6 where \( N = 64 \) and \( m = n = p = 4 \)), so that equation (61) holds. The potential is that of equation (62):

\[
V_r = \begin{cases} 
-\zeta & (r=1,m,k) \\
0 & (r\neq1,m,k)
\end{cases} \quad \text{(mod. N)} \tag{62a}
\]

\[
J_r = \begin{cases} 
-\zeta & (r=1,m,k) \\
0 & (r\neq1,m,k)
\end{cases} \quad \text{(mod. N)} \tag{62b}
\]

where for convenience in notation

\[ k = mn \]

We have, analogous to the two-dimensional case:

\[
\epsilon = 2\theta_1 = 2\theta_m = 2\theta_k = 2\theta_{N-1} = 2\theta_{N-m} = 2\theta_{N-k} = \frac{1}{4} \beta \zeta \quad \text{(261)}
\]

\[
\Delta_r = \delta_{r,1} + \delta_{r,m} + \delta_{r,k} + \delta_{r,N-1} + \delta_{r,N-m} + \delta_{r,N-k} \quad \text{(262)}
\]

\[
a = (x_1 - 1) \quad \text{(263)}
\]

\[
x_r = e^{4\epsilon \Delta_r} = 1 + a \Delta_r \quad \text{(264)}
\]
The partition function is then:

\[
Q = 2 \sum_{n=0}^{[N/2]} T_n
\]

\[
T_n = \cosh \left[ (N-2n) \sqrt{v} \right] x_1^{-3n} t_n \left( 1 - \frac{1}{2} \delta_{n,N/2} \right)
\]

\[
t_n = \frac{1}{n!} \sum_{q_1=1}^{N'} \cdots \sum_{q_N=1}^{N'} \prod_{r=1}^{n} \prod_{s=1}^{n} (1 + a^q (q_r - q_s)) \quad \text{(266a)}
\]

\[
(1+ a^q (q_r - q_s)) \quad \text{for } r < s
\]

In order to evaluate the expansion terms the following sums are required, which differ from the two-dimensional case:

\[
\sum_{q_1 q_2} \Delta (q_1 - q_2) \Delta (q_1 - q_3) = 6 \sum_{q_1 q_2} \Delta (q_1 - q_2) \Delta (q_1 - q_3)
\]

\[
+ \delta (q_1 - q_2), N-1 + \delta (q_1 - q_2), N-m + \delta (q_1 - q_2), N-k = 6N
\]

\[
\sum_{q_1 q_2 q_3} \Delta (q_1 - q_2) \Delta (q_1 - q_3) = \sum_{q_1 q_2} \Delta (q_1 - q_2) \left( \sum_{q_3} \Delta (q_1 - q_3) \right)
\]

\[
= 6 \sum_{q_1 q_2} \Delta (q_1 - q_2) = 36N
\]

\[
\sum_{q_1 q_2 q_3 q_4} \Delta (q_1 - q_2) \Delta (q_1 - q_3) \Delta (q_1 - q_4) = 216N
\]

\[
\sum_{q_1 q_2 q_3} \Delta (q_1 - q_2) \Delta (q_1 - q_3) \Delta (q_2 - q_3) = 0
\]

\[
\sum_{q_1 q_2 q_3 q_4} \Delta (q_1 - q_2) \Delta (q_2 - q_3) \Delta (q_3 - q_4) \Delta (q_1 - q_4) = 90N
\]
\[
\sum q_1 q_2 q_3 q_4 q_5 \Delta (q_1-q_2) \Delta (q_2-q_3) \Delta (q_3-q_4) \Delta (q_4-q_5) \Delta (q_1-q_5) = 0
\] (271)
\[
\sum q_1 q_2 q_3 q_4 q_5 \Delta (q_1-q_2) \Delta (q_1-q_4) \Delta (q_2-q_3) \Delta (q_2-q_4) \Delta (q_3-q_5) = 318N
\] (272)

Equations (269) through (271) are most readily evaluated by a scheme similar to that illustrated in connection with equation (237). They correspond respectively to a triangular bond configuration, a closed quadrilateral, and a pentagon. The last equation represents a bond configuration equivalent to that of Fig. 12(b)(6) and can be evaluated in the same way as equation (244). In determining these sums it was assumed, as in the two-dimensional case, that N\rightarrow \infty so that m<<N and k<<N.

It is now possible to evaluate the terms of the series by expanding the products as in equations (233d),(239) through (242) and (245) through (250), but inserting the values of the \( \Delta \)-product sums appropriate to the 3-dimensional model that were computed above in equations (267) through (272). The considerations leading to these expansions are, as in the two-dimensional case, identical with the topological arguments examined in connection with the one-dimensional system. One obtains in this way:

\[
t_0 = 1
\] (273a)
\[
t_1 = N
\] (273b)
\[
t_2 = \frac{1}{2} \left( \sum q_1 q_2 (1+a\Delta (q_1-q_2) - N) = \frac{N}{2}[N+6x_1-7] \right)
\] (273c)
\[
t_3 = \frac{1}{3!} \left( \sum q_1 q_2 q_3 (1+a\Delta (q_1-q_2))(1+a\Delta (q_1-q_3))(1+a\Delta (q_2-q_3)) \right) - 3\sum q_1 q_2 (1+a\Delta (q_1-q_2))^2 + 2N
\]
\[
= \frac{N}{3!} [N^2+3N(6x_1-7)+90x_1^2-216x_1+128]
\] (273d)
The three-dimensional partition function, correct to this term, is then:

\[
Q = 2A\{\cosh(N\nu) + N\nu^{-3} \cosh[(N-2)\nu]\} + \frac{N}{2!} \nu^{-6}[N^4+6N^2(6x_1-7)+N(468x_1^2-1116x_1+659) + 72x_1^4 + 1992x_1^3
\]

\[
+7884x_1^2+9720x_1-3906]\]
\[ + \frac{N}{5!} x_1^{-15}(N^4+10N^3(6x_1-7)+5N^2(288x_1^2-684x_1+403) \]
\[ + 10N(36x_1^4+1536x_1^3-5868x_1^2+7140x_1-2849) \]
\[ + 240(24x_1^5+213x_1^4-1402x_1^3+2766x_1^2-2304x_1+703) + 24 \]
\[ \cosh[(N-10)v] + \ldots \}

where:

\[ A = \begin{cases} 
\exp(Nv) = y^{N/2} \\
\exp(3Ne) = x_1^{3/4N} 
\end{cases} \text{ (fluid)} \]

\[ \exp(3Ne) = x_1^{3/4N} \text{ (ferromagnet)} \]

One can derive a series expansion of \( Q^{1/N} \) from equation (274) in the same way as in the two-dimensional case with the following result:

\[ Q^{1/N} = K(y,x_1) = A^{1/N} y^{-1/2}(1 + x_1^{-3}y + 3(x_1^{-5} - x_1^{-6})y^2 \]
\[ + 3(5x_1^{-7} - 11x_1^{-8} + 6x_1^{-9})y^3 + (3x_1^{-8} + 83x_1^{-9} - 309x_1^{-10} \]
\[ + 360x_1^{-11} - 137x_1^{-12})y^4 + (48x_1^{-10} + 429x_1^{-11} - 2676x_1^{-12} \]
\[ + 5055x_1^{-13} - 4041x_1^{-14} + 1185x_1^{-15})y^5 + \ldots \}

(276)

The series is valid for \( y \leq 1 \), i.e. \( v \leq 0 \). As in the two-dimensional series, \( y \) is replaced by \( y^{-1} \) and \( y^{-1/2} \) by the factor \( y^{1/2} \) to obtain the corresponding series valid for \( y \geq 1 \) or \( v \geq 0 \).

It is also possible to obtain a series expansion of \( \frac{1}{N} \ln Q \). To do so, we write, as in equations (254) and (255):

\[ Q = [K(y, x_1)]^N = Ay^{-N/2} \sum_{n=0}^{N} a_n(x_1)y^n \]

(277)

Then:

\[ q = \frac{1}{N} \ln(Q) = \ln(K) = \sum_n \alpha_n y^n + \ln C \]

(278)
so that:

\[ Q = \exp\{N \ln (J)\} = C^N \exp\{N \sum_n a_n y^n\} \]

\[ = C^N \left[ 1 + N \sum_n a_n y^n + \frac{1}{2} N^2 (\sum_n a_n y^n)^2 + \ldots \right] \]

\[ = A y^{-N/2} \left[ 1 + \sum_{n=1}^{N} a_n y^n \right] \]

Identifying \( C^N \) with \( A y^{-N/2} \), we have then:

\[ \sum_{n=1}^{N} a_n y^n = \sum_n N^n \tau_n = N \sum_n a_n y^n + \frac{1}{2} N^2 (\sum_n a_n y^n)^2 + \ldots \]

(280)

where \( \tau_n \) is the coefficient of \( N^n \) in (274). Consequently, since \( N \) is arbitrary:

\[ \sum_n a_n y^n = \tau_1 (y, x_1) \]

(281)

That is, we can obtain the coefficients \( a_n \) by comparing powers of \( y \) with the coefficients of \( N \) in (274). In this way we obtain:

\[ q = \frac{1}{N} \ln(A) - v + 1 + x_1^3 y + (3x_1^5 - \frac{7}{2} x_1^6)y^2 \]

\[ + (15x_1^{-7} - 36x_1^{-8} + 21 \frac{1}{3} x_1^{-9})y^3 + (3x_1^{-8} + 83x_1^{-9} \]

\[ - 328 \frac{1}{2} x_1^{-10} + 405x_1^{-11} - 162 \frac{3}{4} x_1^{-12})y^4 \]

\[ + (48x_1^{-10} + 426x_1^{-11} - 2804x_1^{-12} + 5532x_1^{-13} - 4608x_1^{-14} \]

\[ + 1406 \frac{1}{5} x_1^{-15})y^5 + \ldots \]

Comparison of these results with those obtained by other authors by independent methods based on a true three-dimensional model shows perfect agreement in every detail. Thus, Hill (cf. equation (45.1)) gives a low-temperature expansion for the three-dimensional cubic lattice in powers of \( x_1 \). There is complete agreement between his
series and equation (276) above. Hill likewise gives an expansion of $K$ for the three-dimensional lattice (cf. equation (45.6)) which agrees completely with equation (276) above, although he does not include the coefficients of $y^5$. Likewise, Hill's expansion of $q$ (cf. equation (45.3)) is in agreement with equation (282). One must note, however, that Hill's expansion is for $y=1$ and that the last term in his series includes contributions from higher powers of $y$ than are included in (282). Domb\textsuperscript{12} likewise gives series expansions for the three-dimensional model which agree with those above. The most complete series expansion for a three-dimensional ferromagnetic lattice is given by Wakefield\textsuperscript{24}. His expansion likewise agrees term for term with equation (276). In making these comparisons due allowance must, of course, be made for the difference in notation of these authors.
D. Conclusions:

The series expansion of the one-dimensional model with nearest-neighbor interactions shows, by its agreement with the known closed-form solution for that model, that the partition function, equation (178), is indeed a valid solution of the problem posed in Chapter I, or at least one which is valid in the nearest-neighbor approximation.

The expansion furthermore lays the groundwork for equivalent series expansions in higher dimensions, showing how a series solution may be obtained by identical algebraic techniques in all dimensions.

The two and three dimensional series computed by this standard algebraic method from the partition function, equation (178), are in complete agreement with the series expansions obtained for such models by other entirely independent methods. This serves as confirmation, then, of the applicability of the present model and its solution to systems of higher dimensionality but with more restricted molecular interactions, as discussed in Chapter II D (1). The present solution has the advantage of permitting a unified approach to problems of this type regardless of dimensionality. The solution of the series problem, furthermore, was accomplished basically by algebraic techniques. While topological arguments were used to simplify some of the more tedious computations, this is not strictly essential. The method does lend itself to the computation of series expansion coefficients by electronic computer, as Appendix II illustrates. This may prove a useful tool in obtaining solutions to the three-dimensional Ising problem to any desired degree of approximation.

One further advantage of the present method lies in the fact that while the molecular interactions in higher dimensions must be restricted
in order that the present method apply, it is not necessary that interactions be restricted to nearest neighbor ones. One can readily take into account next-nearest neighbor interactions, interactions with neighbors thrice removed, etc. The only restriction is that the number of such interactions remain limited or else the $\Delta$-function products will be too tedious to evaluate. The technique of solution is still identical; the coefficients of the parameter "a" remain invariant to such a change, as do the $\Delta$-products. All that will change is the definition of $\Delta_r$ and the values of the various sums of $\Delta$ products. To illustrate this point briefly, examine equation (209). This expansion is the same in models of all dimensionality and will not be affected by the inclusion of additional bonds. However, the value of the sums of $\Delta$-function products involved varies, viz. equations (203), (205), (235) and (237), (268b) and (270); these are fairly readily evaluated. The crux of the problem is then the finding of the coefficients of $a$; once they are available the problem is essentially solved for all dimensions and all reasonable interactions.

One other interesting conclusion emerges from this analysis: If next-nearest neighbor interactions are included in the two-dimensional square lattice the $\Delta$-functions resulting therefrom assume formally the same appearance as those of the three-dimensional system with nearest-neighbor interactions. This gives further insight, then, into the reason why this augmented problem is not tractable by the Onsager matrix method (cf. Chapter III) and why the addition of such bonds introduces a "nonlinearity" reminiscent of the three-dimensional problem. 11,12
Chapter VII

THERMODYNAMICS OF INFINITE SYSTEMS

In this chapter the thermodynamic behavior of infinite systems will be investigated, i.e. of systems which have been solved by means of the partition function, equation (178), and which are infinite in the sense that the solution is valid for \( N \to \infty \). This means, of course, that either the volume of the system becomes infinite or else the cell parameter goes to zero. These two limits are not equivalent as the first two systems investigated will illustrate.

A. Ideal Gas

Let us assume that the interaction potential between particles of the system is zero, i.e.

\[ V_r = 0 \quad (r=0, 1, \ldots, N-1, N) \quad (283) \]

While we formally set \( V_0 = V_N = 0 \) together with all the other interaction potentials, this does not actually affect the hard-core potential, since that has been built into the model (cf. the discussion following equation (11)). It will be seen presently how this repulsive potential is affected by the process of taking the limit \( N \to \infty \).

The partition function is then (cf. equations (178)):

\[
q_N = 2^N e^{Nv} \{ \cosh(Nv) + N \cosh[(N-2)v] + 1/2 \cosh[(N-4)v] \sum_{q_1=1}^{N'} \sum_{q_2=1}^{N'} \sum_{q_3=1}^{N'} \cdot 1 + \cdots \\
+ 1/3! \cosh[(N-6)v] \sum_{q_1=1}^{N'} \sum_{q_2=1}^{N'} \sum_{q_3=1}^{N'} \sum_{q_3=1}^{N'} \cdot 1 + \cdots \} \\
+ 1/n! \cosh[(N-2n)v] \sum_{q_1=1}^{N'} \cdots \sum_{q_1=1}^{N'} \cdot 1 + \cdots \} = 2^N e^{Nv} \sum_{n=0}^{[N/2]} \frac{N!}{n!(N-2n)!} \cosh[(N-2n)v](1-1/2 \delta n, N/2) \quad (284)
\]
\[ 2^N e^{Nv \cosh N} = (1 + e^{2v})^N \]

The last result follows directly from a derivation analogous to that in equation (188). Thus (cf. equations (27), (32), (34), (36)):

\[ Q_N = (1 + \xi \xi / \lambda)^N = (1 + \xi \xi / \lambda N)^N \]  

(285)

Where \( V \) is the volume of the system. If the system of interest is strictly the one-dimensional chain, then \( V = L \). But as we saw in Chapter III and the last chapter, it is possible to construct two or three dimensional systems from the one-dimensional one by using proper boundary conditions. Since all interactions are zero in this instance, the boundary conditions are trivial. Consequently, \( Q_N \) in equation (284) or (285) may represent a one, two, or three-dimensional system, provided that we choose \( V \) and \( \lambda \) to have the proper dimensionality*.

Since we wish all interactions to go to zero, including the hard core repulsive interaction, we shall simply keep the volume \( V \) large but fixed as \( N \to \infty \). This results in reducing the cell parameter \( \xi \) to zero, so that we are dealing then with point particles without physical dimension. This corresponds, of course, to the concept of an ideal gas. In the limit \( N \to \infty \) the repulsive interaction becomes trivial also. Thus we have:

\[ \lim_{N \to \infty} Q_N = \lim_{N \to \infty} \left( 1 + (V \xi / \lambda) / N \right)^N = \exp(V \xi / \lambda) = Q_\infty \]  

(286)

Hence (cf. equation (180)):

\[ \ln(Q_\infty) = \beta \rho V = V \xi / \lambda = V e^\beta \xi / \lambda \]

From the definition of a grand canonical average or expectation value we have:

\[ \xi \partial (\ln Q_\infty) / \partial \xi = \sum_{n=0}^{\infty} n(\xi / \lambda)^n Z_n / Q_\infty = <n> = V \xi / \lambda \]

*The \( \lambda \) of equation (27) must be generalized in that case to \( \lambda = (\beta h^2 / 2\pi m)^{1/2} \) where \( n \) is the dimensionality of the system.
Combining this with equation (280) we have:

\[ \beta pV = <n> \quad (286a) \]

or

\[ pV = <n> \frac{KT}{mRT} \quad (286b) \]

which is the well-known equation of state of an ideal gas with \(<n>\) the number of particles of the system and \(m\) the number of moles. It should be observed that in obtaining this equation of state we were obliged to let the particles become ideal point particles so as truly to eliminate all interactions.

The thermodynamics of the ideal gas are well known and will not be explored further here.

B. A Fluid of Hard Rods

Suppose that the particles of the system have a finite length \(d\) and that insofar as any interaction between them is concerned the core contained within this length is absolutely impenetrable. We choose the cell parameter \(L\) equal to the particle length, as before. The interaction potential is then:

\[ v_r = \begin{cases} \zeta_{h.c.} = \infty & (r=0) \\ 0 & (r \neq 0) \end{cases} \quad (\text{Mod. } N) \]

where \(\zeta_{h.c.}\) is the hard-core potential. The appropriate Boltzmann factor is:

\[ X_r = \exp[-\beta v_r] = \exp[-\beta \zeta_{h.c.} \delta_{r,0}] = (1-\delta_{r,0}) \]

or

\[ X(q_r-q_s) = (1 - \delta_{q_r,q_s}) \]

We have then for the partition function:

\[ Q_N = 2e^{Nv}[N/2] \sum_{n=0}^{[N/2]} \cosh[(N-2n)v] t_n (1 - 1/2 \delta_{n,N/2}) \quad (287a) \]
The evaluation of the $\delta$-function sums is equivalent to the expansion of the primed sums in the last chapter (cf. equation (197) through (200)) with $f(q_r, q_s) = 1$. This shows once more the way in which the primed summation arises from and is synonymous with the hard-core repulsive potential. Thus we can write for the partition function:

\[
Q_N = 2e^{N\nu} \sum_{n=0}^{[N/2]} (N\choose n) \cosh [(N-2n)\nu] (1-1/2\delta_{n,N/2})
\]

\[
= (y^{N/2}) (y^{-N/2}) \sum_{n=0}^{N} (N\choose n) y^n = \sum_{n=0}^{N} (N\choose n) y^n = (1+y)^N
\]

\[
= (1+e^{2\nu})^N = (1+\frac{\xi}{\lambda})^N
\] (287b)

which is of the same form as that for the ideal gas, equation (285).

However, there is one vital difference: in the ideal gas case, in deriving the equation of state we let the cell parameter go to zero. In the present instance this is not permissible, since we have specified that the particles are of finite length, having a repulsive core. The effect of this upon the derivation of the equation of state is decisive.

Before proceeding it will be observed that the intermediate step in the derivation of equation (287b) has an obvious physical interpretation:

\[
\sum_{n=0}^{N} (N\choose n) y^n = \sum_{n=0}^{N} (N\choose n) \exp[2\nu] = \sum_{n=0}^{N} (N\choose n) (\frac{\xi}{\lambda} \exp[\beta g])^n
\]

\[
= \sum_{n=0}^{N} 1/n! N(N-1)(N-2)\cdots(N-n+1) \xi^n \lambda^{-n} \exp[n\beta g]
\]
\[
\sum_{n=0}^{N} \frac{1}{n!} N^{n} (N_{2} - \epsilon) (N_{2} - 2\epsilon) \cdots (N_{2} - (n-1)\epsilon) \lambda^{-n} \exp[n\beta g]
\]

\[
\sum_{n=0}^{N} \frac{1}{n!} \lambda^{-n} \exp[n\beta g] L(L-d)(L-2d) \cdots (L-(n-1)d)
\]

which is seen to be the grand-canonical partition function of a system of hard rods with the usual "volume" term \(L^n\) replaced by the corresponding free volume equivalent.

It is also possible to show in this connection that adoption of a cell parameter smaller than the particle dimension \(d\) is a trivial variation of the scheme used here, i.e. of letting the cell parameter \(\lambda_o\) equal the particle dimension. Suppose, then, that \(\lambda_o < \lambda\) and that each particle occupies

\[m' = [-d/\lambda_o]\]

(288)
cells, where \([\cdot]\) means "nearest integer equal to or less than". The entire system has now \(N/\lambda_o = K\) cells, where \(K > N\). Assuming for convenience that \(m'\) is odd, we have:

\[m = 1/2(m'-1)\]

(289)

and can write the potential in the form:

\[V_r = \begin{cases} \zeta \text{ h.c.} & (r=0,1,2,\ldots,m) \quad (\text{Mod. } N) \\ 0 & (r\neq0,1,2,\ldots,m) \quad (\text{Mod. } N) \end{cases}\]

(290)

Then:

\[x_r = (1-\delta_{r,0} - \delta_{r,1} - \cdots - \delta_{r,m} - \delta_{r,N-1} - \cdots - \delta_{r,N-m})\]

(291)

\[t_n = 1/n! \sum_{q_1=1}^{K} \cdots \sum_{q_n=1}^{K} 1-\delta_{q_r,q_s} - \delta_{q_r,q_s+1} - \delta_{q_r,q_s+2} - \cdots - \delta_{q_r,q_s+m}\]

(292)
\[
K = \frac{1}{n!} \sum_{q_1=1}^{K} \cdots \sum_{q_n=1}^{K} (1-m')^n \delta_{q_1, q_2, \ldots, q_n} = \frac{1}{n!} K(K-m')(K-2m') \cdots (K-(n-1)m')
\]
since all \(\delta\)-functions are equivalent in this sum. Letting now \(K=Nm'\) this becomes (we shall require that \(N\) be an integer by choosing \(\xi_0\) so that \(m'\) is a factor of \(K\)):
\[
t_n = \frac{1}{n!} Nm' (Nm'-m') (Nm'-2m') \cdots (Nm'-(n-1)m') = \left(\begin{array}{c} N \\ m' \end{array}\right)^n
\]
\[(293)\]
The partition function is then:
\[
Q_N = \sum_{n=0}^{K} \left(\begin{array}{c} N \\ n \end{array}\right) (m')^n y^n = \sum_{n=0}^{m'} \left(\begin{array}{c} N \\ n \end{array}\right) \eta^n
\]
\[(294)\]
where
\[
\eta = m'y = m' \exp[2\nu] = m' \xi_0 / \lambda, \quad \xi = (d/\lambda) \xi
\]
\[(295)\]
Observe that \(\left(\begin{array}{c} N \\ n \end{array}\right) = 0\) if \(n > N\). Since \(m'>1\), the upper limit of the sum is greater than \(N\). Thus we can write
\[
Q_N = \sum_{n=0}^{N} \left(\begin{array}{c} N \\ n \end{array}\right) \eta^n = (1+\eta)^N = \left(1 + \frac{d}{\lambda} \xi\right)^N
\]
\[(296)\]
But this is the same result as (287b) above, which we obtained by choosing the cell parameter \(\xi\) equal to the particle diameter \(d\).
Consequently a choice of cell parameter \(\xi\) smaller than the particle size is a trivial variation of the present choice, as asserted.

From equation (287b) one obtains then:
\[
\ln Q_N = N \ln (1 + \frac{d}{\lambda} \xi)
\]
\[(297)\]
Therefore (cf. equation (281)):
\[
\xi \frac{\partial}{\partial \xi} Q_N = \frac{N}{1+\xi} \left(\frac{d}{\lambda}\right) \xi = \langle n \rangle
\]
\[(298)\]
Or
\[
\rho = \frac{\langle n \rangle}{N} = \frac{\left(\frac{d}{\lambda}\right) \xi}{1+\xi}
\]
\[(299)\]
The quantity \( \rho \) may be thought of as the proportion of the line occupied by particles, for we can write

\[
\rho = \langle n \rangle / N = \langle n \rangle \xi / N \xi = L_0 / L
\]

(300)

where \( L_0 = \langle n \rangle \xi = \langle n \rangle d \) is the total length of the line of total length \( L \) occupied by particles. Alternatively, one can think of \( \rho \) as a dimensionless density, related to the normal density \( \bar{\rho} = 1/v \) by (cf. equations (50) and (52)):

\[
\rho = \xi / (L / \langle n \rangle) = \xi / v
\]

(301)

From equation (299) we have then:

\[
d / \lambda \xi = \rho / (1 - \rho)
\]

(302)

Substituting this in (297) one obtains:

\[
\ln Q_N = \ln \left[ \left( 1 + \frac{\langle n \rangle}{N(1 - \rho)} \right)^N \right] = \ln \left[ \left( 1 + \frac{\langle n \rangle}{N(1 - \rho)} \right)^N \right]
\]

(303)

And

\[
\lim_{N \to \infty} \ln Q_N = \ln Q_\infty = \lim_{N \to \infty} \ln \left[ \left( 1 + \frac{\langle n \rangle}{N(1 - \rho)} \right)^N \right] = \ln \exp \left[ \langle n \rangle / (1 - \rho) \right]
\]

\[
= \langle n \rangle / (1 - \rho) = \beta \rho L
\]

(304)

Consequently, the equation of state is:

\[
pL(1 - \rho) = \langle n \rangle KT = mRT
\]

(305)

which is the Tonks equation of state for a fluid of hard rods.\(^{23}\)

The factor \( \rho \), as observed above, represents the proportion of the line occupied by particles. Consequently \( (1 - \rho) \) is the proportion of the line not occupied by particles and hence \( L(1 - \rho) \) is the net "volume" (i.e., length of line) available to the system.

As in the perfect gas case, the thermodynamics are sufficiently well known that it is not worthwhile to derive them again.

Before leaving this system let us inquire what would change in the preceding derivation if the fluid under consideration were a

\^The symbol \( \rho \) used above corresponds to \( \theta \) in Tonks' equation of state.
two or three dimensional one. To be specific, consider a three-dimensional system. We again choose the cell parameter equal to the particle size, in this case the particle diameter. Since the hard core repulsive potential is still the only interaction in the system, this is also given by equation (285). Hence the partition function in equation (287) remains valid, i.e. the sum of \( (1-\delta_{qr,qs}) \) products or the equivalent primed sums still account for the interactions of the system. Consequently the remainder of the derivation holds as well. Only the cell itself has changed. Since we are now dealing with a three-dimensional system, the basic particles are three-dimensional and so is, of course, the basic cell, being a tiny cube of dimensions \( l \times l \times l \). As previous analysis pointed out, the three-dimensional system is formed by "wrapping" these strings, (i.e., essentially one-dimensional systems but with the string having breadth and depth) around a four-dimensional torus. Equation (303) holds unchanged, but in equation (304) we must now substitute \( V \) for \( L \) as the volume of the system, giving as the equation of state:

\[
pV(1-\rho) = \langle n \rangle KT = mRT
\]

(306)

The partition function, equation (178), thus leads to the correct equation of state for a fluid of hard rods, hard disks, or hard spheres.

C. A One-Dimensional Fluid with Nearest-Neighbor Interactions

This section deals with the thermodynamic properties of a one-dimensional fluid comprised of particles with a hard-core repulsive potential and nearest-neighbor attractive interactions. While such a fluid may only have limited applicability, it has the advantage of being mathematically tractable. The analysis points up several
interesting parallels with real fluids.

In Chapter VI the partition function of this system was derived in the form:

\[ Q_N = 2 \exp[N\nu]\{\cosh(N\nu) + \sum_{n=1}^{N/2} \sum_{k=1}^{N/n} \left(\frac{N-n-1}{n}\right)_k \frac{1}{\cosh((N-2n)\nu)}\} \]
\[ \cdot \left(1 - \frac{1}{2} \delta_n, N/2\right) \]

It is proved in Appendix V that this is equivalent to (cf. equation (V-17)):

\[ Q_N = \exp[N\nu] \cosh^N\nu\{(1 + \sqrt{1+w})^N + (1 - \sqrt{1+w})^N\} \]
\[ w = (x_1^{-1} - 1) \sech^2\nu \]

Then

\[ \lim_{N \to \infty} \frac{1}{N} \ln Q_n = q = \nu + \ln(\cosh\nu) \]
\[ + \ln(1+\sqrt{1+w}) + \lim_{N \to \infty} \ln\left[1 + \left(\frac{1-\sqrt{1+w}}{1+\sqrt{1+w}}\right)^N\right] \]
\[ = \nu + \ln(\cosh\nu) + \ln(1+\sqrt{1+w}) = \beta p \]

The density (cf. equations (48) through (56) and (299)) is then:

\[ \rho = \frac{\langle n \rangle}{N} = \frac{1}{N} \mathbb{I}[\partial/\partial x (1n_\omega)] = \mathbb{I}(\partial q/\partial x)_\beta = \mathbb{I}(\partial q/\partial x)_\beta(\partial x/\partial x)_\beta \]
\[ = 1/2 \left(\partial q/\partial x\right)_\beta = 1/2 \left(1 + \tanh\nu/\sqrt{1+w}\right) \]

\[ \nu = 1/2 \ln(2X_1 /\lambda) + 1/2 \ln \xi = \nu(\xi, x_1, T) \]

Equation (309) gives the density parametrically as a function of \( \nu \), which in turn is a function of the interaction potential, chemical potential, and temperature. For fixed \( T \) and \( x_1 \), \( \rho \) thus varies with the chemical potential (cf. equation (32)). There exists clearly the following correspondence:
It is then possible to consider $\nu$ as a parameter and to plot pressure versus density from the two parametric equations (308) and (309). Instead, it is more convenient to plot $q$ versus $\rho$, since for a given temperature $q$ is directly proportional to the pressure. The computer program at Appendix VI computes $q$ and $\rho$ for a range of values of the parameter $\nu$ and for various potentials of the Lennard-Jones type (cf. equation (2)). The results are plotted in the graphs, Figure 13. For comparison, the corresponding $q-\rho$ curve for the Tonk's fluid, i.e. for $x_i=1$, is also shown. The graphs indicate clearly that for given temperature and density, the pressure of the system is reduced by an increase in the attractive interaction potential. It is also apparent from the graphs that the one-dimensional fluid with nearest-neighbor interactions only has no phase transition. This is, of course, a well-known result.\textsuperscript{1,3,11,12}

We wish next to compute the isothermal compressibility of the system. This is given by

$$K_T = -\frac{1}{\nu} \left( \frac{\partial \rho}{\partial \rho} \right)_B = -\rho/\xi \left( \frac{\partial \rho}{\partial \rho} \right)_B = 1/\rho \left( \frac{\partial \rho}{\partial \rho} \right)_B$$

$$= 1/\rho \left( \frac{\partial \rho}{\partial \rho} \right)_B \left[ (1/\beta^2) \left( \frac{\partial q}{\partial \nu} \right)_B \right] = (\beta^2/2\rho^2) \left( \frac{\partial \rho}{\partial \nu} \right)_B$$

(310a)

where equation (309) was used. Now,

$$\left( \frac{\partial \rho}{\partial \nu} \right)_B = x_i^{-1} \text{sech}^2 \nu / [2(1+w)^{3/2}]$$

Hence

$$K_T = (\xi/4K) x_i^{-1} \text{sech}^2 \nu / [\rho^2 T (1+w)^{3/2}]$$

(310b)
PRESSURE VS. DENSITY
ONE-DIMENSIONAL SYSTEM
WITH NEAREST-NEIGHBOR INTERACTIONS $\gamma/k = 64.0$

FIG. 13A(1)
PRESSURE VS. DENSITY
ONE-DIMENSIONAL SYSTEM
WITH NEAREST-NEIGHBOR
INTERACTIONS \( T = 13.34^\circ \)
1-DIM.
SYSTEM
\( \gamma = 64 \text{K} \)
This quantity is of interest, since it reflects the fluctuations in the density of the system:

\[
\sum_{n=0}^{N} \frac{(\xi/\lambda)^n}{\sigma} \sum \exp\left[-(Nq + \beta U_c)\right] = 1
\]  

(311a)

\[
\sum_{n=0}^{N} \left[n-N\xi(\partial q/\partial \xi)_{\beta}\right] (\xi/\lambda)^n \sum \exp\left[-(Nq + \beta U_c)\right] = 0
\]  

(311b)

\[
\sum_{n=0}^{N} \left\{\sum_{\sigma} [n-N\xi(\partial q/\partial \xi)_{\beta}] (\xi/\lambda)^n \sum \exp\left[-(Nq + \beta U_c)\right] \right\}
\]

\[
= \sum_{n=0}^{N} \left\{\sum_{\sigma} \exp\left[-(Nq + \beta U_c)\right]\right\} = 0
\]  

(311c)

Or

\[
N\xi(\partial q/\partial \xi)_{\beta} = N/2 \quad (\partial q/\partial \rho)_{\beta} = \frac{(n-\langle n \rangle)^2}{\beta L} = \frac{n^2}{\beta L} - \frac{n^2}{\rho^2}
\]

(311d)

Consequently:

\[
K_T = (\beta L/N\rho^2)(\langle n^2 \rangle - \langle n \rangle^2) = \beta L(\langle n^2 \rangle/\rho^2 - 1)
\]

(312)

Density fluctuations are, of course, intimately associated with phase transitions where the density in both phases changes discontinuously. Thus the compressibility provides a sensitive indicator of phase transitions. This is also apparent from the fact that

Slope of \(p-p\) diagram = \(1/(\rho K_T)\)

and thus the compressibility would be expected to show a discontinuity at the transition point.

Graphs of \(K_T\) versus \(\rho\), plotting values computed by the program at Appendix VI, appear in Figure 14A. Figure 14B contains similar graphs of \(K_T\) versus \(T\). Both sets of graphs show that the compressibility is a monotonic function of both the density and the temperature in this
COMPRESSIONIBILITY

VS.

DENSITY

ONE-DIM. SYSTEM

WITH NEAREST-NEIGHBOR

INTERACTIONS \( \gamma/k = 64 \)

\( T = 8^\circ K \)

\( T = 13.34^\circ K \)

\( T = 32^\circ K \)
COMPRESSIBILITY VS. DENSITY
ONE-DIMENSIONAL SYSTEM
WITH NEAREST-NEIGHBOR
INTERACTIONS  \( T = 13.34^\circ K \)
COMPRESSIBILITY

VS.

TEMPERATURE

$g/k = 64$

$\rho = \frac{1}{2}$

1-DIM. SYSTEM

FIG. 14B
system, thus confirming once more that a one-dimensional system with only nearest-neighbor interactions cannot have a phase transition.

The internal energy of the system can be determined as follows:

\[ U = \langle H \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{n=0}^{N} H \exp[-(Nq+\beta H)] = -N(\partial q/\partial \beta) \xi \]  

(313a)

so that the internal energy density, i.e. the internal energy per cell is:

\[ u = U/N = -(\partial q/\partial \beta) \xi = -[(\partial q/\partial \nu)_{\beta}(\partial \nu/\partial \beta) + (\partial q/\partial \beta)_{\nu}] \]  

(313b)

\[ = -2(\partial q/\partial \beta) \xi + (\partial q/\partial \beta)_{\nu} \]

\[ \xi = (1/2)(\partial q/\partial \beta) \ln(2\pi m) = 1/2 \ln \beta + 1/2 \ln \xi + (1/2)\beta \xi \]

\[ = -1/4 \beta + \xi/2 \]

\[ (\partial q/\partial \beta)_{\nu} = -(\xi x_1^{-1} \text{sech}^2 \nu/[2\sqrt{1+w}(1+\sqrt{1+w})] \]

Therefore

\[ u = \rho KT/2 - \xi \left[ \rho - \frac{x_1^{-1} \text{sech}^2 \nu}{2\sqrt{1+w}(1+\sqrt{1+w})} \right] \]  

(313c)

Figure 15 is a plot of internal energy versus temperature, while in Figure 16 internal energy is plotted versus density. Computations were made by the program at Appendix VI. It is apparent from this equation as well as from the plot that the ground state of this fluid is \( u_0 = -\xi \rho \).

The following considerations serve to check the validity and meaning of the last term. Let us define a long-range order parameter (cf. equations (48) through (53)).

---

Let \( q = q(\nu, \beta) ; \nu = \nu(\beta, \xi) \). Then \( dq = [(\partial q/\partial \nu)_\beta]d\nu + [(\partial q/\partial \beta)_\nu]d\beta \) ;

\[ d\nu = [(\partial q/\partial \beta)_\xi]d\xi + [(\partial q/\partial \xi)_\beta]d\xi \] so that \( dq = [(\partial q/\partial \nu)_\beta][(\partial \nu/\partial \beta)_\xi]d\beta \)

\[ + [(\partial q/\partial \nu)_\beta][(\partial \nu/\partial \xi)_\beta]d\xi + [(\partial q/\partial \beta)_\nu]d\beta \). Equation (313b) follows now directly.
INTERNAL ENERGY VS. TEMPERATURE
ONE-DIMENSIONAL SYSTEM
WITH NEAREST-NEIGHBOR INTERACTIONS
DEPTH = 64K

TOTAL INTERNAL ENERGY

CONFIGURATIONAL
INTERNAL ENERGY
INTERNAL ENERGY VS. DENSITY
ONE-DIMENSIONAL SYSTEM
WITH NEAREST-NEIGHBOR INTERACTIONS \( s/k = 64 \)

![Graph showing internal energy vs. density with lines for different temperatures.]

- T = 32°
- T = 13.34°
\[ L = \frac{1}{N} < \sum_{K=1}^{N} \sigma_K > = \frac{1}{N} (N_+ - N_-) = \frac{2N_+}{N} - 1 \]

\[ = 2\langle n \rangle /N - 1 = 2\rho - 1 \quad (314) \]

where \( N_+ \) and \( N_- \) have the meaning defined in connection with equation (22). The term long-range order parameter seems appropriate since \(|L|\) is an indicator of the order of the system: if \(|L| = 1\), the system is either completely occupied or empty. If half the cells are occupied, then \(|L| = 0\). Values of \(|L|\) such that \(0 < |L| < 1\) indicate intermediate states of order. We define next the following quantities:

\( N_{++} = \) Total number of nearest-neighbor cells with both cells occupied.

\( N_{--} = \) Total number of nearest-neighbor cells with both cells empty.

\( N_{+-} = \) Total number of nearest-neighbor cells with one cell occupied and one empty.

The following relations hold between these quantities, as is readily seen:

\[ 2N_{++} + N_{+-} = 2N_+ \quad (315) \]

\[ 2N_{--} + N_{+-} = 2N_- \quad (316) \]

And, of course:

\[ N_{++} + N_{--} + N_{+-} = N \]

Let us define also a short-range-order parameter:

\[ \sigma = \frac{1}{N} < \sum_{K=1}^{N} \sigma_K \sigma_{K+1} > = \frac{1}{N} (N_{++} + N_{--} - N_{+-}) \]

\[ = 1 - N_{+-}/N = 1 + 4N_{++}/N - 4N_+/N = 1 + 4n - 4\rho \quad (317) \]

where

\[ n = \frac{N_{++}}{N} \quad (318) \]
as is readily seen, reflects the proportion of neighboring cells that are occupied (empty) if the central cell is occupied (empty). It can be determined from the partition function as follows (cf. equations (35) through (38)):

\[
\sigma = \frac{C_{N/N}}{\sum_{N} \left\{ \prod_{K=1}^{N} \sigma_k \sigma_{K+1} \right\} \exp \left\{ \sum_{K=1}^{N} \sigma_k \sigma_{K+1} \right\}} / q_N
\]

\[
= \frac{1}{N} \frac{3}{\partial \varepsilon} \left( \ln \Xi_N \right)_\partial = \frac{1}{N} \frac{3}{\partial \varepsilon} \left( \ln C_N^{-1} \right)_\partial
\]

\[
= \frac{\partial}{\partial \varepsilon} \left\{ \varepsilon + \ln \cosh \nu + \ln (1 + \sqrt{1 + w}) \right\}_\partial = 1 - \frac{2x_1^{-1} \text{sech}^2 \nu}{\sqrt{1 + w}(1 + \sqrt{1 + w})} (319)
\]

The configurational energy of the system is given by equation (17):

\[
U_c = \frac{1}{4} \sum_{r=1}^{N} \sum_{s=1}^{N} (1 + \sigma_r)(1 + \sigma_{r+s}) \phi_s
\]

where

\[
\phi_s = \frac{1}{2} \left( V_s + V_{N-s} \right) = -\zeta / 2 \left( \delta_{s,1} + \delta_{s,N-1} \right)
\]

Substituting (321) into (320) and carrying out the summation over s one obtains:

\[
U_c = -\zeta \left[ \frac{N}{4} + \frac{N}{2} (2\rho - 1) + \frac{1}{4} \sum_{r=1}^{N} \sigma_r \sigma_{r+1} \right]
\]

\[
= -\zeta \left[ N\rho - \frac{N}{4} + \frac{N}{4} \left( 1 - \frac{2x_1^{-1} \text{sech}^2 \nu}{\sqrt{1 + w}(1 + \sqrt{1 + w})} \right) \right]
\]

\[
= -N \zeta (\rho - \left[ x_1^{-1} \text{sech}^2 \nu \right] / \left[ 2\sqrt{1 + w}(1 + \sqrt{1 + w}) \right]) (322)
\]

The energy density of the system \( u_c = U_c / N \) is therefore exactly the configurational part of the expression \( (313c) \). We observe also that in equation (322)(cf. equation (317) and (318)):

\[
N/4 + N\rho - N/2 + 1/4 < \sum_{r=1}^{N} \sigma_r \sigma_{r+1} > = -N/4 + N\rho + (N/4)\sigma
\]

\[
= N\eta = N++
\]

so that
\[ U_c = -\zeta N^* \]  
(323)

represents just the interaction of all nearest-neighbor occupied cells, as one would expect on physical grounds.

From equation (313) it is now possible to compute the specific heat of the system. We have for the specific heat at constant volume:

\[ C_v = (\partial u/\partial T)_v = (\partial u/\partial T)_\rho = -k B^2 (\partial u/\partial \beta)_\rho \]

\[ = -k B^2 \left[ (\partial u_1/\partial \beta)_\rho + (\partial u_2/\partial \nu)_\beta (\partial \nu/\partial \beta)_\rho + (\partial u_2/\partial \beta)_\nu \right] \]  
(324)

where*

\[ u_1 = \rho KT/2 - \rho \zeta \]

\[ u_2 = \zeta x_1^{-1} \left[ \text{sech}^2 \nu \right] / \left[ 2\sqrt{1+w(1+\sqrt{1+w})} \right] \]  
(325)

For the various partial derivatives one obtains:

\[ (\partial u_1/\partial \beta)_\rho = -\rho/2 \beta^2 \]  
(326a)

\[ (\partial u_2/\partial \nu)_\beta = -\xi x_1^{-1} \frac{\text{sech}^2 \nu \tanh \nu}{2(1+w)^{3/2}} \frac{\left( 2(1+\sqrt{1+w}) + w \right)}{(1+\sqrt{1+w})^2} \]  
(326b)

\[ (\partial u_2/\partial \beta)_\nu = -\left( \xi^2 x_1^{-1} / 4 \right) \frac{\text{sech}^2 \nu}{(1+w)^{3/2}} \frac{\left[ 1+w + \text{tanh}^2 \nu (1+2\sqrt{1+w}) \right]}{(1+\sqrt{1+w})^2} \]  
(326c)

\[ (\partial u_2/\partial \beta)_\rho = -1/2 \xi \tanh \nu \]  
(326d)

Combining these various results, one has for the specific heat:

\[ C_v = k \rho/2 + \frac{1}{4} K (\beta \xi)^2 x_1^{-1} \frac{\text{sech}^4 \nu}{\sqrt{1+w(1+\sqrt{1+w})^2}} \]  
(327)

The specific heat, like the compressibility, is of interest as an indicator of phase transitions. In the case of the specific heat

*The relationship between partial derivatives that was used here follows directly from the footnote on page 166. Taking the derivative of the second equation there we have: \((\partial q/\partial \beta)_\xi = (\partial q/\partial \nu)_\beta (\partial \nu/\partial \beta)_\xi + (\partial q/\partial \beta)_\nu\) which is equivalent to (324).
the connection lies in the fact that this parameter is directly proportional to the energy fluctuations of the system, as a derivation akin to equation (311) will readily show. Such fluctuations are likely to be large near a transition temperature, as is obvious from physical considerations. Onsager's solution of the two-dimensional Ising model shows also that the specific heat has a logarithmic singularity at the Curie temperature. Experimental evidence seems to confirm that there is a singularity of this type at the critical point.

In the present model we find from equation (327) that for a density $\rho=1/2$, the specific heat reduces to:

$$C_V(\rho=1/2) = \frac{K}{4} + \left(\frac{K}{16}\right)(\beta\zeta)^2 \text{sech}^2\left(\frac{\beta\zeta}{4}\right)$$

(328a)

or, letting $\beta\zeta/4 = \phi$:

$$C_V(\rho=1/2) = \frac{K}{4} + K\phi^2 \text{sech}^2\phi$$

(328b)

Or

$$C_V(\rho=1/2)/K - 1/4 = \phi^2 \text{sech}^2\phi$$

(328c)

For $T \to 0$, $\phi \to 0$, but $\lim_{\phi \to \infty} \phi^2 \text{sech}^2\phi = 0$.

Similarly, as $T \to \infty$, $\phi \to 0$, and so $(C_V/K - 1/4)$ is zero at $T=0$ and $T=\infty$.

Since $\phi^2 \text{sech}^2\phi \to 0$, it follows that $(C_V/K - 1/4)$ has a maximum. This maximum is found by solving the equation

$$\phi \tanh \phi = 1$$

(329)

as a quick calculation shows. Numerical approximation indicates that the equation is satisfied to a very good approximation by $\phi=1.2$, which corresponds to

$$T_m = 0.208\xi/K$$

(330)

For the potential $\xi/K=64$ which will be used frequently later (cf. Chapter VIII) this corresponds to a temperature of $13.3^\circ K$. Figure 17 shows a qualitative plot of the specific heat for $\rho=1/2$. Accurate
Figure 17. Specific Heat Versus Temperature.

graphs of the specific heat versus temperature and density are shown in Figures 18 and 19 respectively. The data were computed by the program at Appendix VI from equation (327).

While the specific heat exhibits a maximum, there is no phase transition at that temperature, as the corresponding $q$ vs. $\rho$ diagram shows; nor is there any indication of unusual behavior in the compressibility. Thus, in the one-dimensional system with nearest-neighbor interactions, the specific heat maximum reflects large energy fluctuations, but is not associated with a phase transition.

It is possible to eliminate the parameter $v$ in the equation of state and to write the pressure as an explicit function of the density, temperature, and potential. We start from equation (309):

$$p = \frac{1}{2} \left[ 1 + \tanh \frac{1}{\sqrt{1+v}} \right]$$  (309)

Hence, using equation (307):

$$(2\rho-1) = \frac{\sinh v}{\sqrt{\sinh^2 v + x_1^{-1}}} = \frac{1}{\sqrt{1 + x_1^{-1}/\sinh^2 v}}$$  (331)

Then:
SPECIFIC HEAT

VS.

TEMPERATURE

$\varphi = 64 K; \psi = \frac{1}{2}$
SPECIFIC HEAT V.S. DENSITY
ONE-DIMENSIONAL SYSTEM
WITH NEAREST-NEIGHBOR
INTERACTIONS \( \gamma / K = 64 \)

FIG. 19
\[
\sinh^2 v = \frac{(\rho-1/2)^2}{x_1 \rho (1-\rho)} \\
\cosh^2 v = \frac{[(\rho-1/2)^2 + x_1 \rho (1-\rho)]}{[x_1 \rho (1-\rho)]} \\
e^v = \frac{[(\rho-1/2) + \sqrt{(\rho-1/2)^2 + x_1 \rho (1-\rho)}]}{[x_1^{1/2} \sqrt{1-\rho}]} \\
\]

By substitution in (308) one obtains then:

\[
\beta p_L = \lim_{N \to \infty} \ln \left( 1 + \frac{(\rho-1/2) + \sqrt{(\rho-1/2)^2 + x_1 \rho (1-\rho)}}{x_1 (1-\rho)} \right)^N \\
= \lim_{N \to \infty} \ln \left[ 1 + \frac{(\rho-L/2)^2 + \sqrt{(\rho-L/2)^2 + x_1 <n>(L/2-<n>)}}{x_1 (1-\rho)} \right]^N \\
= \frac{(\rho-L/2)^2 + \sqrt{(\rho-L/2)^2 + x_1 <n>(L/2-<n>)}}{x_1 (1-\rho)} \\
\]

so that

\[
p_{\text{eff}}(1-\rho) = p_{\text{eff}} = KT \frac{1}{x_1} \left[ (\rho-L/2)^2 + \sqrt{(\rho-L/2)^2 + x_1 <n>(L/2-<n>)} \right] \\
\]

Or:

\[
p_{\text{eff}}(1-\rho) = p_{\text{eff}} = KT \frac{1}{x_1} \left[ (\rho-1/2) + \sqrt{(\rho-1/2)^2 + x_1 \rho (1-\rho)} \right] \\
\]

It will be observed that (334a) and (334b) reduce correctly to the equation of state of a fluid of hard rods (cf. equation (305)) when the potential goes to zero, i.e. \( x_1 \to 1 \):

\[
p(x_1=1) = (KT/\xi_{\text{eff}}) \rho = (KT/\xi)(\rho/1-\rho) \\
\]

Equation (335) suggests that one might write equation (334b) in the following way:

\[
p_{\text{eff}} = KT \frac{\rho_{\text{eff}}}{x_1} \\
\]

where:

\[
\rho_{\text{eff}} = \left[ (\rho-1/2) + \sqrt{(\rho-1/2)^2 + x_1 \rho (1-\rho)} \right] x_1^{-1} \\
\]

so that \( \rho_{\text{eff}} \) is an effective density which merges into the true density as the interaction potential goes to zero. Conversely, as the strength of the interaction increases, the effective density decreases, thus
reducing the pressure of the system as compared with the pressure of a system of hard rods at the same temperature*. Figure 13 shows clearly that this is indeed the case.

It is also possible to write the equation of state of the one-dimensional nearest-neighbor fluid in the form of a van-der-Waals equation of state. We have from (334a)

\[(pL)(1-\rho)/\left\{x_1^{-1} [(1-L/2L_0)+\sqrt{(1-L/2L_0)^2+x_1(L/L_0-1)}]\right\} = \langle n \rangle KT\]

where \(L_0 = \langle n \rangle \xi \) is the actual average length of the line occupied by particles of the system. Then:

\[(p+a)(L-b) = \langle n \rangle KT\]

where:

\[a = p\left\{x_1/[1-L/2L_0]+\sqrt{(1-L/2L_0)^2+x_1(L/L_0-1)}\right\}^{-1}\]

\[b = L_0 = \langle n \rangle \xi = L_0\]

The effect of the hard-core repulsion is contained in \(b\), while \(a\) reflects the effect of the attractive potential. It is readily shown that \(a > 0\).

This form of the equation of state also lends itself to a virial expansion. We can write:

\[\sqrt{(\rho-1/2)^2+x_1(1-\rho)} = 1/2 \sqrt{1+4a\rho(1-\rho)} = 1/2 \sum_{n=0}^{\infty} \left(\frac{1/2}{n}\right)^n [4a\rho(1-\rho)]^n\]

\[= 1/2(1+2a\rho(1-\rho)-2a^2\rho^2(1-\rho)^2 + 4a^3\rho^3(1-\rho)^3-10a^4\rho^4(1-\rho)^4+\cdots)\]

\[\text{where} \quad a = (x_1-1)\]

Therefore:

*The term "pressure" is used here and in what follows to simplify comparison with systems of higher dimensionality. Actually, one must remember that the pressure of a one-dimensional system is a force.
\[ p = \frac{(KT/\zeta)(x_1^{-1})[(\rho-1/2)+\sqrt{(\rho-1/2)^2+x_1\rho(1-\rho)}]}{(1-\rho)} \]  

\[ p = \rho KT[1 + (2-x_1)\rho + (4-5x_1 + 2x_1^2)\rho^2 + (8-18x_1 + 16x_1^2 - 5x_1^3)\rho^3 + (16-56x_1 + 82x_1^2 - 55x_1^3 + 14x_1^4)\rho^4 + (32-160x_1 + 340x_1^2 - 365x_1^3 + 196x_1^4 - 42x_1^5)\rho^5 + \ldots] \]

Or

\[ p = \rho KT[1 + x_1^{-1} \sum_{k=2}^{\infty} \frac{(1 + 2\sum_{n=2}^{\infty} (-1)^{n+1} (2n-3)!a^n \rho^{k-1}}{(n-2)! (m-n)! (2n-m)!}] \]

\[ a = \begin{cases} 
2n & \text{if } 2n \leq k \\
\frac{k}{2} & \text{if } 2n > k 
\end{cases} \]  

(399b)

It is easily verified that when the potential vanishes, i.e. when \( x_1+1 \), this reduces correctly to

\[ p = \rho KT(1 + \sum_{k=1}^{\infty} \rho^k) = KT(\rho/1-\rho) \]

Figure 20 is a plot of the second virial coefficient in the above expansion versus temperature. Also shown is a graph of the true virial coefficient for a three-dimensional fluid. The resemblance between these two curves is rather surprising in view of the difference in dimension.

The internal energy density of the system, expressed as a function of the density takes the form:

\[ u = \rho KT/2 - \rho \zeta \left[ 1 - 2(1-\rho)/[1+2\sqrt{(\rho-1/2)^2+x_1\rho(1-\rho)}] \right] \]  

(340)

While it is, of course, possible also to express the compressibility and specific heat as a function of \( \rho \), the form of these expressions is more complicated than the parametric equations. For the specific heat one has, for instance:

\[ C_v = \frac{1}{2} k\rho + 2k(\beta\zeta)^2 \left( \frac{\rho(1-\rho)}{1+2\sqrt{(\rho-1/2)^2+x_1\rho(1-\rho)}} \right)^2 \left( \frac{x_1}{\sqrt{(\rho-1/2)^2+x_1\rho(1-\rho)}} \right) \]  

(341)
SECOND VIRIAL COEFFICIENT FOR ONE-DIMENSIONAL FLUID

TRUE SECOND VIRIAL COEFFICIENT
For \( \rho=1/2 \) this reduces once more to the previous expression.

\[
C_v(\rho=1/2) = K/4 + K/16 (\beta\xi)^2 \text{sech}^2(\beta\xi/4)
\]  
(328)

This can be rewritten in a way which shows explicitly that the specific heat approaches zero as \( T \to 0 \). We have:

\[
(C_v - K/4) \big|_{\rho=1/2} = K/4 (\beta\xi)^2 \frac{x_1^{-1/2}}{(1+x_1^{-1/2})^2}
\]

\[
= K \eta^2 \exp[-1/\eta] \sum_{r=0}^{\infty} (-1)^{r+1} r \exp[-(r-1)/\eta]
\]

\[
= K/\eta^2 \exp[-1/\eta] (1-\exp[1/\eta])
\]

\[
= K/\eta^2 \exp[-1/\eta] (\eta \ll 1)
\]

where

\[
\eta = 2KT/\xi
\]

Thus the specific heat is seen to approach zero exponentially as \( T \to 0 \), i.e. faster than the \( T^3 \) law of Debye.\(^{27}\)

The chemical potential of the system is readily obtained from the relation (cf. equations (32), (34), (36), and (332)):

\[
\exp[2\psi] = \frac{([\rho-1/2]+\sqrt{(\rho-1/2)^2+x_1\rho(1-\rho)})^2/[x_1\rho(1-\rho)]}{(\xi x_1)/\lambda \exp[\beta g]}
\]

Hence:

\[
g = K T \ln(\lambda/\lambda) + 2 K T \ln([\rho-1/2]+\sqrt{(\rho-1/2)^2+x_1\rho(1-\rho)})/[x_1\rho(1-\rho)]
\]

(344a)

It is easily verified that this explicit relationship between chemical potential and density is in accord with the range of values shown in Table 3. One can also verify that as the interparticle potential vanishes, the above expression reduces to

\[
g(\gamma=0) = g_0 = K T [\ln(\lambda/\lambda)+\ln(\rho/1-\gamma)]
\]

(345)

which is the correct form for the Tonks fluid of hard rods. Equations (344a) and (345) are the chemical potential per particle. The chemical
potential for the entire system is then given by
\[ G = \langle n \rangle g \]  
(344b)

while the chemical potential density is
\[ \gamma = \rho g \]  
(343c)

The entropy of the system can be determined from the relation:
\[ s = S/N = 1/T (u + \rho \chi - \gamma) = k_B u + k q - k_B \gamma \]  
(346a)

\[ = k_B u + k q - 2k_B \nu + k_B \ln (\lambda/\nu) + k_B \rho \zeta \]
\[ = k [1/2\rho + \nu(1-2\rho) + \ln(\cosh\nu) + \ln(1+\sqrt{1+\theta})] \]
\[ + \beta \nu x_1^{-1} \cdot \frac{\text{sech}^2\nu}{2/\sqrt{1+\theta}(1+\sqrt{1+\theta})} + \rho \ln(\lambda/\nu)] \]

where equations (308), (313), and (343) were used. In terms of equation (334) and (340), the entropy can also be written in the form:
\[ s = 1/2 \ k_B + 2k_B \zeta \left( \frac{\rho(1-\rho)}{1+2\sqrt{(\rho-1/2)^2+\nu^2}\rho(1-\rho)} \right) \]
\[ + k \left( \frac{\rho_{eff}}{1-\rho} \right) - 2k_B \ln \left[ \frac{\rho_{eff}}{\sqrt{\rho(1-\rho)}} \right] + \rho_B \ln(\lambda/\nu) \]  
(346b)

where equation (336b) was used. The entropy of the entire system is, of course,
\[ S = N s \]  
(347a)

while the entropy per particle is given by
\[ S_p = S/\langle n \rangle = s/\rho \]  
(347b)

As the interaction goes to zero, i.e. as \( x \rightarrow 1 \), one recovers from equation (346) the entropy density of a fluid of hard rods:
\[ S_0 = 1/2 \ k_B + k(\rho/1-\rho) - k_B \ln(\rho/1-\rho) + k_B \ln(\lambda/\nu) \]  
(348a)

The entropy per particle is in this case (using (347)):
\[ S_{p0} = 1/2 \ k + k(1-\rho)^{-1} - k_B \ln(\rho/1-\rho) + k_B \ln(\lambda/\nu) \]  
(348b)

It is readily verified that
\[ \lim_{\rho \to 0} S_{\rho_0} = \lim_{\rho \to 1} S_{\rho_0} = +\infty \]

By virtue of the relation\(^1,2,3\)

\[ W = \exp[-S/k] \]

\((W\) being the probability of finding the system in a given state), the entropy in equation (348b) gives the correct probability of finding the system in either of these extreme states. From the same equation we find that for the fluid of hard rods:

\[ \frac{\partial S_{\rho_0}}{\partial \rho} = k \frac{(2\rho - 1)\rho(1-\rho)}{(1-\rho)^2} = 0 \]

yields \(\rho_{\text{max}} = 1/2\), as one would expect since there are more microstates available to the system at \(\rho = 1/2\) than at any other density. With an attractive interaction potential, however, it becomes energetically advantageous for the particles of the system to cluster closer together. This tendency is, of course, partially offset by rapid increase in pressure experienced by the system at higher densities resulting from the kinetic interaction. One would nevertheless expect that with an attractive interaction, there would be a shift in the maximum probability toward higher densities. Figure 21A presents a plot of specific entropy (entropy per particle) versus density for a hard-rod fluid \((x_1^{-1} = 1)\) and for a fluid with an attractive interaction potential. The figure shows that such a shift in maximum probability toward higher densities does in fact occur.

Figure 21B is a plot of entropy density (entropy per cell) versus system density for three different interaction potentials. The curves were computed from equation (346a). One easily finds from equation (346a) that

\[ \lim_{\rho \to 0} S = \lim_{\rho \to 1} S = 0 \]
ENTROPY VS. DENSITY
1-DIM. SYSTEM
WITH NEAREST-NEIGHBOR INTERACTIONS

FIG. 21A
Figure 21B reflects this behaviour and also shows a shift toward higher densities of the entropy extremum as the attractive interaction becomes stronger.

The preceding analysis of the one-dimensional system reflects many parallels with the behavior of real fluids. But there is, of course, no phase transition except for a degenerate one at $T=0$. Thus, equation (310b) shows that the $p-\rho$ curve has a horizontal tangent at $T=0$, while (334) indicates $p=0$ at $T=0$ for all values of the density except $\rho=1$.

In the limit $\rho\rightarrow 1$ we have from (308):

$$\lim_{T\rightarrow 0} p = \lim_{g\rightarrow \infty} p = \lim_{T\rightarrow 0} \frac{KT}{2v} = \lim_{T\rightarrow 0} \frac{KT}{2v} [\frac{1}{2} \ln T + \zeta/KT + g/KT]$$

$$+ \text{finite terms} = \lim_{T\rightarrow 0} \frac{KT}{2v} \ln T + \lim_{g\rightarrow \infty} g/KT + \text{finite terms}$$

$$= \infty$$

At $T=0$ the system therefore behaves as if it were actually undergoing a phase transition, as shown in Figure 22.

![Figure 22. Degenerate Phase Transition of the One-Dimensional Fluid with Nearest-Neighbor Interactions](image)
ENTROPY DENSITY
VS.
SYSTEM DENSITY
ONE-DIMENSIONAL SYSTEM
WITH NEAREST-NEIGHBOR FORCES

T = 24°K
These conclusions are supported by an analysis of the analyticity of this system. In accordance with the discussion of Chapter V, this analysis involves finding the zeros of the partition function (cf. equation (307)):

\[ Q_N = \exp[Nv] \cosh^N(v) [(1+\sqrt{1+w})^N + (1-\sqrt{1+w})^N] = 0 \]  

But \( \exp[Nv] \neq 0 \) except for \( v \to \infty \); and since one finds readily that

\[ \lim_{v \to \infty} Q_N = 1 \], equation (349) requires that

\[ \cosh^N(v) [(1+\sqrt{1+w})^N + (1-\sqrt{1+w})^N] = 0 \]  

Or, writing \( w \) out explicitly (cf. equation (307)):

\[ \cosh^N(v) [(1+\sqrt{1+(x_1^{-1} - 1)\text{sech}^2v})^N + (1-\sqrt{1+(x_1^{-1} - 1)\text{sech}^2v})^N] = 0 \]

Let

\[ (x_1^{-1} - 1)\text{sech}^2v = -\text{sech}^2\eta \]  

Then the above equation can be rewritten:

\[ (1-x_1^{-1})^{N/2} \cosh^N \eta [(1+\tanh\eta)^N + (1-\tanh\eta)^N] \]

\[ = (1-x_1^{-1})^{N/2} (\exp[N\eta] + \exp[-N\eta]) = 2(1-x_1^{-1})^{N/2} \cosh(N\eta) = 0 \]

This equation is clearly satisfied by

\[ \cosh(N\eta) = 0 \text{, or } N\eta = (2k-1)\frac{\pi}{2}; \text{ (}k=1,2,3,\ldots\text{)} \]  

If we define

\[ \eta = i\phi \]  

the zeros of the partition function are given by:

\[ \phi_k = \frac{2k-1}{2N} \pi \]  

From equation (351) we have then:

\[ |\cosh(v_k)| = \sqrt{1-x_1^{-T}} |\cosh_n| = \sqrt{1-x_1^{-T}} |\cos \phi_k| \leq \sqrt{1-x_1^{-T}} \leq 1 \]  

But \( |\cosh(v_k)| \leq 1 \) implies \( v_k = iv_k \). Therefore we have immediately,

\[ y_k = \exp[2v_k] = \exp[2iv_k] \]
in consonance with the theorem of Yang and Lee quoted in Chapter V, i.e. the zeros all lie on the unit circle in the complex $y$-plane. It follows from the above relations that:

$$\cosh(v_k) = \cos(v_k) = \sqrt{1-x_1^{-1}} \cos(\phi_k)$$

(358a)

or

$$v_k = \cos^{-1} \left[ \sqrt{1-x_1^{-1}} \cos \left( \frac{2k-1}{2N} \pi \right) \right], \quad (k=1,2,\ldots,N) \quad (358b)$$

We must observe that the angle $V_k$ lies in what in Chapter V was called the complex $x$-plane. The corresponding angle in the complex $y$-plane is related to $V_k$ by:

$$\alpha_k = 2V_k \quad (359)$$

It is now immediately apparent that the zeros on the unit circle in the $y$-plane cannot approach arbitrarily close to the real axis. Thus we have for $k=1$, $\lim_{N \to \infty} \cos(1/2N \pi) = 1$, so that the value $k=1$ gives the value of $\phi$ which permits the closest approach to the real axis from above. Likewise, for $k=N$ we have $\lim_{N \to \infty} \cos[(1-1/2N)\pi] = -1$, so that this value permits the closest approach to the real axis in the $y$-plane from below (which in the $x$-plane corresponds to approaching the negative $x$-axis from above). Thus the angle of closest approach in the $y$-plane is:

$$\alpha_k(\text{min}) = 2v_k(\text{min}) = 2\cos^{-1}(\sqrt{1-x_1^{-1}}) \quad (360)$$

One notes that for $x_1^{-1}=1$, $\alpha_k=\pi$, which agrees with the earlier analysis in Chapter V that all $N$ roots of the Tonks fluid are degenerate and lie at $y=-1$. The positive real $y$-axis can be reached only if $x_1^{-1}=0$. But this implies either that $T \to 0$, which corresponds to the degenerate phase transition examined above; it can also be satisfied by an infinitely
deep potential well. This leads to the same type of degenerate phase transition, as is apparent from equation (334). As the size of the system increases, i.e. as $N \to \infty$, the density of zeros on the unit circle increases until in the limit it becomes continuous. This is shown in Figure 23. It becomes possible then to define a distribution function $g(a)$ such that

$$\lim_{N \to \infty} \frac{1}{N} \int_{0}^{2\pi} g(a) \, da = 1 = \frac{2}{N} \int_{0}^{\pi} g(a) \, da$$

(361)

where the symmetry of the zeros, resulting from their occurrence in complex-conjugate pairs, was used.

Figure 23. Distribution of Zeros of the Partition Function on the Unit Circle.
Since in the limit as $N \to \infty$ we can think of the index $k$ in (358) as a continuous variable, we can write: $g(\alpha) = \frac{\partial}{\partial \alpha}$. And from (358) one has:

$$-\sin(v) \frac{\partial v}{\partial \alpha} = -\sqrt{1-x_1^{-1}} \sin(\phi)(2\pi/N) \frac{\partial k}{\partial \alpha}$$

so that

$$g(\alpha) = \frac{\partial}{\partial \alpha} = \frac{N \sin(v)}{2\pi \sqrt{1-x_1^{-1}} \sin \phi} = \frac{N \sin(\alpha/2)}{2\pi \sin^2(\alpha/2) - x_1^{-1}}$$

$$= \frac{N \tanh(v)}{2\pi \sqrt{1+w}} = \frac{N}{2\pi} (2\rho-1)$$

where equation (309) was used. If we now write the partition function in terms of its roots, we obtain:

$$Q_N = A \prod_{k=1}^{[N/2]} (1-y/\exp[i\alpha_k]) = A \prod_{k=1}^{[N/2]} (1-y \exp[i\alpha_k](1-y \exp[-i\alpha_k]))$$

$$= A \prod_{k=1}^{[N/2]} (1 - 2y \cos(\alpha_k) + y^2)$$

so that

$$\ln Q_N = \ln A + \sum_{k=1}^{[N/2]} \ln(1-2y \cos(\alpha_k) + y^2)$$

$$= \ln A + \sum_{k=1}^{N} \ln(1 - 2y \cos(\alpha_k) + y^2)^{1/2}$$

And:

$$\frac{p_0}{kT} = \lim_{N \to \infty} \frac{1}{N} \ln Q_N = a + \lim_{N \to \infty} \frac{2}{N} \int_0^\pi g(\alpha) \ln(1-2y \cos \alpha + y^2)^{1/2} d\alpha$$

where

$$a = \lim_{N \to \infty} \frac{1}{N} \ln A$$

and equation (361) was used. Substituting the distribution function, equation (362) and taking account of the angle $\alpha_{\text{min}}$ shown in Figure 23, we have:
\[
\frac{pE}{KT} = a + \frac{1}{2\pi} \int_{\alpha_{\text{min}}}^{\pi} \frac{\sin(\alpha/2)}{\sqrt{\sin^2(\alpha/2) - x_1^{-1}}} \ln \left(1 - 2y \cos(\alpha) + y^2\right) d\alpha
\]  
(365)

Letting \(\cos(\alpha/2) = bw\), this becomes:

\[
\frac{pE}{KT} = a + \frac{b}{\pi} \int_{0}^{1} \frac{dw}{\sqrt{1 - bw - x_1^{-1}}} \cdot \ln[1 + 2y + y^2 - 4yb^2w^2]
\]

Choosing \(b = \sqrt{1 - x_1^{-1}} = \cos(1/2 \alpha_{\text{min}})\) we have

\[
\frac{pE}{KT} = a + \frac{1}{\pi} \int_{0}^{1} \frac{dw}{\sqrt{1+w^2}} \ln[(1+y)^2 - \gamma w^2] = a + I_1 + I_2
\]

(366a)

where

\[
I_1 = \frac{1}{\pi} \int_{0}^{1} \frac{\ln(1-\gamma w^2)}{\sqrt{1-w^2}} dw
\]

(366b)

\[
I_2 = \frac{2}{\pi} \ln(1+y) \int_{0}^{1} \frac{dw}{\sqrt{1-w^2}}
\]

\[
\gamma = \frac{4y(1-x_1^{-1})}{(1+y)^2}
\]

Integral \(I_2\) is elementary, while \(I_1\) can be integrated (cf. ref. 28, p. 562, (29)) to yield:

\[
I_1 = \ln[(1+\sqrt{1-\gamma})/2]
\]

One obtains then:

\[
\frac{pE}{KT} = a + \ln[1/2(1+y) + 1/2\sqrt{(1+y)^2 - 4y(1-x_1^{-1})}] \\
= a + \ln\{\exp[v]\cosh(1+\sqrt{1+(x_1^{-1})}\text{sech}^2v)\}
\]

(367)

which is the partition function given by equation (308) with \(a = 0\), i.e. \(A=1\). By considering the analyticity of the partition function one thus obtains valuable insight into the thermodynamic behavior of the system, as pointed out by Yang and Lee, and can determine the partition function and hence the equation of state providing the distribution of zeros is known.
D. A Fluid with Infinite-Range Interactions

In this section we shall consider a fluid with an attractive potential of infinitely long range, i.e. a potential where the range parameter, \( \gamma \), (cf. equation (2)) goes to zero. A comparable magnetic potential in which all exchange interactions are identical has been applied by Kittel to a Heisenberg ferromagnet. In the case of a fluid, such a potential has no physical counterpart; however, it constitutes an interesting limiting case to systems with interaction potentials of increasingly longer range. We noted in the preceding chapter that in considering systems with nearest-neighbor interactions, additional full-strength nearest-neighbor interactions appeared as we increased the dimensionality of the system, i.e. as we added more nearest neighbors. The system to be considered now could be thought of as a limiting case to a sequence of nearest-neighbor systems of increasingly higher dimensionality. Alternatively it can be viewed as the limit of a sequence of one-dimensional systems with intermolecular potentials of increasingly long range, i.e. with Lennard-Jones potentials where the range parameter, \( \gamma \), approaches zero.

The potential we wish to consider is:

\[
V(x) = \begin{cases} 
+\infty & (x \leq \xi) \\
-\zeta & (x > \xi) 
\end{cases} 
\]  

The corresponding periodic, discrete potential appropriate to the partition function, equation (178), is:

\[
V_r = \begin{cases} 
0 & (r=0) \\
-\zeta & (r\neq0) 
\end{cases} \pmod{N} 
\]  

Other pertinent parameters are (cf. equations (36) and (156)): 
\[ X_r = \exp[\beta \Theta_r] = \exp[-\beta (V_r + V_{N-r})] \]  
\[ = \begin{cases} 
1 & (r=0) \\
\exp[2\beta \xi] & (r \neq 0)
\end{cases} \quad (\text{mod. } N) \]  
\[ \Theta = \sum_{r=1}^{N} \frac{1}{4} \beta (N-1) \xi 
\]

The partition function, equation (178), then takes the form:

\[ Q_N = 2^N A \sum_{n=0}^{[N/2]} \cosh[(N-2n)\nu] \exp[-\beta n(N-1)\xi \Theta_n] (1 - \frac{1}{2} \delta_{n,N/2}) \] (371)

\[ t_0 = 1 
\]
\[ t_n = \frac{1}{n!} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \prod_{r=1}^{n} \prod_{s=1}^{n} X(q_r-q_s) 
\]
\[ = \frac{1}{n!} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \exp[2 \sum_{r=1}^{n} \sum_{s=1}^{n} \beta \xi] 
\]
\[ = \frac{1}{n!} \exp[n(n-1)\beta \xi] \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \cdot 1 = \binom{N}{n} \exp[n(n-1)\beta \xi] \]

Hence we have for the partition function:* 

\[ Q_N = A \sum_{n=0}^{N} \binom{N}{n} \exp[-\beta n(n-1)\xi \Theta_n] \cosh[(N-2n)\nu] \] (373)

\[ = A \sum_{n=0}^{N} \binom{N}{n} \chi^{-n(n-1)} \exp[(N-2n)\nu] \]

\[ = Ay^{-N/2} \sum_{n=0}^{N} \binom{N}{n} y^n x^{-n(N-n)} \]

where \( y \) is defined by equation (194), and 

\[ x = \exp[\beta \xi] \] (374)

Although the sum in (373) looks suggestive, it is not readily evaluated. One can, however, determine the thermodynamic parameters of interest numerically. For a fluid (cf. equation (178)) \( A = 2 \exp[\nu] \), so that:

*Since \( Q_N \) is invariant to the substitution \( n \to (N-n) \)
\[ q = \frac{p\ell}{KT} = \frac{1}{N} \ln[Q_N] = \nu + \frac{1}{N} \ln \left\{ \sum_{n=0}^{N} \binom{N}{n} x^{-n(N-n)} \cosh[(N-2n)\nu] \right\} \]  

(375)

The density is given by:

\[ \rho = 1/2 \left( \frac{\partial q}{\partial \nu} \right)_\beta = 1/2[1 + T_\nu/NT] \]  

(376)

where:

\[ T(\nu,x) = \sum_{n=0}^{N} \binom{N}{n} x^{-n(N-n)} \cosh[(N-2n)\nu] \]  

(377a)

\[ T_\nu(\nu,x) = \sum_{n=0}^{N} \binom{N}{n} (N-2n)x^{-n(N-n)} \sinh[(N-2n)\nu] \]  

(377b)

The compressibility of the system can be found as follows (cf. equation (310)):

\[ (\partial \rho/\partial \nu)_\beta = 1/2 \left[ \frac{T_\nu}{NT} - \frac{1}{N} (T_\nu/T)^2 \right] = 1/2 \left[ \frac{T_\nu}{NT} - (2\rho-1)^2 N \right] \]  

(378)

where:

\[ T_\nu = \sum_{n=0}^{N} \binom{N}{n}(N-2n)x^{-n(N-n)} \cosh[(N-2n)\nu] \]  

(379)

Then:

\[ K_T = (\beta\ell/4\rho^2) \left[ \frac{T_\nu}{NT} - (2\rho-1)^2 N \right] \]  

(380)

The internal energy is (cf. equation (313)):

\[ U = -\left[ (\partial q/\partial \nu)_\beta (\partial \nu/\partial \beta)_\xi + (\partial q/\partial \beta)_\nu \right] \]  

(381)

\[ = 1/2 \rho KT - (N-1)\rho \xi + \zeta(T_\nu/NT) \]  

\[ = 1/2 \rho KT - \zeta[(N-1)\rho - (T_\nu/NT)] \]  

\[ = u_1 + u_2 \]

where

\[ T_\chi = -(\partial T/\partial x)_\nu = \sum_{n=0}^{N} \binom{N}{n} n(N-n) x^{-n(N-n)} \cosh[(N-2n)\nu] \]  

(382)
The specific heat is found as in equations (324) through (327):

\[ C_v = -k \beta^2 \left( \frac{\partial u_1}{\partial \beta} \rho + \frac{\partial u_2}{\partial \beta} \nu \frac{\partial v}{\partial \beta} \rho + \frac{\partial u_2}{\partial \beta} \nu \right) \]  

(384a)

\[ \frac{\partial u_1}{\partial \beta} \rho = -\rho/2\beta^2 \]  

(385a)

\[ \frac{\partial u_2}{\partial \beta} \nu = (\zeta/N)\left[ \frac{T_{\chi\nu}}{T} - (2\rho-1)(N\Gamma_{\chi}/T) \right] \]  

(385b)

\[ T_{\chi\nu} = -\left[ \frac{\partial^2 T}{\partial x \partial \nu} \right] = \sum_{n=0}^{N} \binom{N}{n} n(N-n)(N-2n)x^{-n(N-n)} \sinh[(N-2n)\nu] \]  

(385c)

\[ \frac{\partial \nu}{\partial \beta} \rho = \zeta \left[ \frac{(2\rho-1)N\Gamma_{\chi} - T_{\chi\nu}}{(2\rho-1)N\Gamma_{\nu} - T_{\nu\nu}} \right] \]  

(385d)

\[ \frac{\partial u_2}{\partial \beta} \nu = (\zeta^2/N)\left[ \frac{(T_{\chi}/T)^2 - T_{\chi\chi}/T} \right] \]  

(385e)

\[ T_{\chi\chi} = \frac{\partial^2 T}{\partial x^2} = \sum_{n=0}^{N} \binom{N}{n} n^2(N-n)^2x^{-n(N-n)} \cosh[(N-2n)\nu] \]  

(385f)

Then:

\[ C_v = \frac{1}{2} k\rho + k(\beta \zeta)^2 \left\{ \frac{1}{NT} \left[ \frac{(2\rho-1)N\Gamma_{\chi} - T_{\chi\nu}}{(2\rho-1)N\Gamma_{\nu} - T_{\nu\nu}} \right]^2 \right\} \]  

(384b)

\[ + \frac{1}{NT^2} \left[ T \frac{T_{\chi\chi}}{x} - T_{\chi\chi}^2 \right] \}

The pressure, density, compressibility, and specific heat of this system have been computed from equations (375), (376), (380), and (384b) by means of the computer program at Appendix VII. Computer runs proved feasible for systems with up to 240 cells. Figure 24 is a plot of the specific heat curves obtained in this way for systems...
SPECIFIC HEAT
VS
TEMPERATURE

ONE-DIMENSIONAL SYSTEM
WITH
INFINITE-RANGE INTERACTIONS
\gamma = 0.00 \quad \text{DEPTH} = 64.00
\rho = \frac{1}{2}

\begin{align*}
1000 & \quad 1.0 \quad 0.0 - 20 \quad N = 50 \\
2000 & \quad 1.3835^\circ \quad 1233.75^\circ \quad N = 100 \\
3000 & \quad 2.3713^\circ \quad 2637.73^\circ \quad N = 200 \\
4000 & \quad 4.3249^\circ \quad 5558.49^\circ \quad N = 240 \\
5000 & \quad 6.7298^\circ \quad 6729.81^\circ \quad \text{SGT}
\end{align*}

FIG. 24

TEMPERATURE
ranging from 10 cells to 240 cells. It appears from the graphs that
the maxima tend toward some sort of limit, although it is not clear
from an inspection of the graphs what this limit is. However, analysis
of the following table suggests that \( \lim_{N \to \infty} N \beta N = 2. \)

<table>
<thead>
<tr>
<th>( N )</th>
<th>( T_m ) ((^0K))</th>
<th>( \beta = N \tau / KT_m )</th>
<th>( \Delta (N \beta)/\Delta N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>193.95</td>
<td>3.30</td>
<td>0.038</td>
</tr>
<tr>
<td>20</td>
<td>438.35</td>
<td>2.92</td>
<td>0.0076</td>
</tr>
<tr>
<td>50</td>
<td>1233.76</td>
<td>2.69</td>
<td>0.0052</td>
</tr>
<tr>
<td>100</td>
<td>2637.53</td>
<td>2.43</td>
<td>0.0013</td>
</tr>
<tr>
<td>200</td>
<td>5558.49</td>
<td>2.30</td>
<td>0.0005</td>
</tr>
<tr>
<td>240</td>
<td>6729.81</td>
<td>2.28</td>
<td></td>
</tr>
</tbody>
</table>

The validity of this surmise will be examined further below. It is
also apparent from Figure 24 that the specific heat curves assume a
characteristic shape. A typical experimental specific heat curve is
shown qualitatively in Figure 25. It is based on curves for \( \beta \)-brass and
\( \text{Au Cu}_3 \) obtained by Nix and Shockley*.25 One sees that such a curve
rises at first gradually, then more steeply to a maximum (which ideally
is probably infinitely high, although this has not been proved experi-
mentally); the curve then drops off very much more sharply and very
gradually tails off to an asymptotic value at infinity. It is quite
apparent that the curves in Figure 24 approach such a shape. As the

*The two alloys to which this curve applies exhibit typical order-
disorder phase transitions that are akin, mathematically, to the phase
transition of a ferromagnet and hence also to those of a fluid. All
of them, like any order-disorder transition, are amenable to analysis.
by means of the Ising formalism. One would therefore suppose that the
specific heat curves display qualitatively similar shapes.
size of the system is increased, the curves rise to higher peaks, then fall off more sharply and thereafter gradually approach an asymptotic value.*

The grand potential of the system, \( q=pT/KT \), is plotted against density in Figure 26. The curves are in fact isotherms of pressure versus density, since the pressure is directly proportional to the grand potential when the temperature is constant. It is obvious from the graph that the isotherm of the larger system is to all intents and purposes that of a fluid undergoing a phase transition. While the slope of the horizontal portion of the curve is not quite zero, it is very nearly so. The isotherm of a smaller system, \( N=20 \), is shown for comparison; it shows plainly how a true phase transition is approached with increasing size of the system. Isotherms for systems of intermediate size are not shown in order not to make the graph confusing. Such isotherms occupy intermediate positions between the

*The asymptotic value of 0.25 arises, of course, from the term \( \frac{1}{2} \, kT \) in equation (384b), with \( p = 1/2 \).
PRESSURE VS. DENSITY ISOHERMS
ONE-DIMENSIONAL SYSTEM
WITH
INFINITE-RANGE INTERACTIONS
$\gamma/k = 64$, $j = 0.0$

$N = 240$, $T = 8000^\circ$
$N = 240$, $T_c = 6729.81^\circ$
$N = 20$, $T = 438.35^\circ$

Fig. 26

Squares to the inch
two shown. It is interesting to note that the present model leads to the correct isotherm for a phase transition without the necessity of using the Maxwell construction.¹

Figure 27 is a plot of the compressibility versus density for the 240 cell system. The compressibility curve exhibits anomalous behavior that is in consonance with the incipient phase transition visible in Figure 26. The computer data do not give the height of the maximum nor the exact shape of the intervening curve.

It is possible to generalize and confirm the computer results by an analysis of equation (373). To do so we wish to find the maximum term in the series:

\[
Q_N = \sum_{n=0}^{N} A \left( \frac{x}{n} \right)^n \cosh[(N-2n)v] = \sum_{n=0}^{N} T_n(x,v)
\]

(373)

Let us designate this term by \( T_m \); we can then write:

\[
Q_N = A T_m \left[ 1 + \sum_{n=0}^{m-1} \left( \frac{T_n}{T_m} \right) + \sum_{n=m+1}^{N} \left( \frac{T_n}{T_m} \right) \right]
\]

(386)

so that:

\[
q = \lim_{N \to \infty} \frac{1}{N} \ln Q_N = v + \lim_{N \to \infty} \frac{1}{N} \ln T_m + R
\]

(387a)

where \( R \) is a remainder term:

\[
R = \lim_{N \to \infty} \frac{1}{N} \ln \left( 1 + \sum_{n} \frac{T_n}{T_m} \right)
\]

(388)

There are \( N \) terms in the sum appearing in the argument of the logarithm, and \(|T_n/T_m| \leq 1\). Thus

\[
|R| = \lim_{N \to \infty} \frac{1}{N} \left| \ln \left( 1 + \sum_{n} \frac{T_n}{T_m} \right) \right| \leq \lim_{N \to \infty} \frac{1}{N} \ln N = \mathcal{O}(1)
\]
COMPRESSIBILITY VS. DENSITY
1-DIM. SYSTEM WITH
INFINITE-RANGE POTENTIAL
\( \gamma/\lambda = 64; \gamma = 0.0 \)
\( N = 240 \)
In the limit \( N \to \infty \) we can therefore neglect the remainder term, and thus have that\(^1,2\)

\[
q = v + \lim_{N \to \infty} \frac{1}{N} \ln(T_m) \tag{387b}
\]

It therefore suffices to find the maximum term of the series (373) in order to be able to determine the thermodynamic behavior of the system, and in particular the phase transition of interest here. We saw in Chapter V that such transitions occur in the vicinity of the point \( y = \exp[2v] = 1 \), i.e. \( v = 0 \) which by virtue of equations (376) and (377) corresponds to a density of \( \rho = 1/2 \). Thus we can confine our attention to finding the maximum term of the series

\[
\sum_{n=0}^{N} \binom{N}{n} x^{-n}(N-n) = T_n(x,0)
\]

The combinatorial symbol is not very convenient to use in what follows, and we shall replace it by the Stirling approximation. For this to be valid, we assume that the index \( m \) will turn out to be such that \( m \to \infty \) as \( N \to \infty \), and confirm later that this condition is met. We must then maximize:

\[
T_n(x,0) = \exp\left\{ N \ln N - N - n \ln n + n - (N-n)\ln(N-n) + (N-n)-n(N-n)\beta \gamma \right\} \tag{389}
\]

Clearly the exponential is a maximum when the exponent is a maximum, so that it suffices to maximize:

\[
F(N, n, \beta, \gamma) = N \ln N - N - n \ln n + n - (N-n)\ln(N-n) + (N-n)-n(N-n)\beta \gamma
\]

which requires that

\[
\frac{\partial F}{\partial n} = \ln(N/n - 1) + (2n - N)\beta \gamma = 0 \tag{390a}
\]

Let \( n/N = r \), then

\[
\ln(1/r - 1) + (2r - 1) N\beta \gamma = 0 \tag{390b}
\]
Or:

\[ r = (1 + \exp[-(2r-1)N\delta])^{-1} = \frac{\exp[1/2(2r-1)N\delta]}{\exp[1/2(2r-1)N\delta] + \exp[-1/2(2r-1)N\delta]} \]

\[ = \frac{1}{2} \left\{ 1 + \tanh \left[ \frac{1}{2}(2r-1)N\delta \right] \right\} \quad (391) \]

so that

\[(2r-1) = \tanh\left[ \frac{1}{2}(2r-1)N\delta \right] \quad (392)\]

This is a transcendental equation for \( r \). One obvious solution is

\[(2r-1)=0, \text{ i.e. } r=1/2.\]  

By virtue of equation (387), all thermodynamic properties follow from the maximum term \( T_m \) in the limit \( N\rightarrow \infty \). Thus in that limit:

\[
\lim_{N\rightarrow \infty} r = \lim_{N\rightarrow \infty} n/N = \lim_{N\rightarrow \infty} \langle n \rangle/N = \rho \quad (393)
\]

Consequently, the solution \((2r-1)=0\) corresponds to a density \( \rho=1/2 \).

This (cf. equations (376) and (377)) is the normal density corresponding to \( \nu=0 \). If the system is to have a phase transition, however, the density must be a multiple-valued function of the pressure and hence of \( \nu \). If there is a phase transition, therefore, there must be other solutions of equation (392). Let us write the equation in the form

\[ x = \tanh(ax) \quad (394a) \]

and attempt to solve it graphically from the two equations

\[ y = x \]

\[ y = \tanh(ax) \quad (394b) \]

Figure 28 is a qualitative plot of these two equations. Intercept \( I_1 \) is the solution corresponding to \( \rho=1/2 \), i.e. \((2\rho-1)=x=0\). It is clear from the figure that there can be two other solutions corresponding to \((2\rho-1)=\pm x_1\), i.e. \( \rho=1/2 \pm 1/2 x_1 \). The graph shows these additional solutions can exist if and only if the curve \( y=\tanh(ax) \) has a slope at the origin greater than that of the straight line \( y=x \); i.e. we must
require that
\[
y' = a \text{sech}^2(ax) \bigg|_{x=0} = a = \frac{1}{2} N_\beta \zeta > 1
\] (395)

Consequently, if \( \frac{1}{2} N_\beta \zeta < 1 \) there can be no phase transition, while if \( \frac{1}{2} N_\beta \zeta > 1 \), there are three values of \( \rho \) that correspond to \( \nu = 0 \). In the latter case there is then a phase transition with the isotherm having the qualitative appearance shown in Figure 29. It is apparent that the critical, or Curie temperature must be defined by:

\[
a_c = \frac{1}{2} N_\beta \zeta = \frac{N\zeta}{2K_T} = 1
\] (396a)

Or:
\[
N_\beta \zeta = \frac{N\zeta}{K_T} = 2
\] (396b)

This confirms the earlier surmise based on analysis of Figure 24 that the sequence \( \{N_\beta \zeta\} \) has a limit \( \sim 2 \). Equation (396b) shows that this limit is 2. The critical temperature is then
Figure 29. Isotherm with Phase Transition* (Qualitative)

\[ T_c = \lim_{N \to \infty} \frac{N \varepsilon}{2k} = \infty \]  

(396c)

Consequently, a macroscopic system (system with infinite volume, i.e. an infinite number of cells) would exhibit a phase transition at any temperature. For finite systems, the preceding conclusions hold only approximately, since then \( T_m \) (cf. equation (387)) is no longer the only significant term; one must also consider the remainder term. For \( N \ll \infty \) the critical temperature is finite. The following table shows the critical temperatures determined by computer and the corresponding temperature from equation (396a) if that equation held for finite \( N \) (which it does only very approximately):

<table>
<thead>
<tr>
<th>( N )</th>
<th>( T_c ) (computes)</th>
<th>( T_c ) (equ. 396)</th>
<th>( T_c ) (comp.)/( T_c ) (equ. 396)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>193.95</td>
<td>320</td>
<td>0.60</td>
</tr>
<tr>
<td>20</td>
<td>438.35</td>
<td>640</td>
<td>0.68</td>
</tr>
</tbody>
</table>

*See Fig. 28 for the meaning of \( x_1 \).
An analysis identical to that leading to equation (390) shows then that the quantity to be maximized is:

$$f = N \ln N - \frac{N}{n} \ln n + n - (N-n) \ln (N-n) + (N-n)$$

Then

$$\partial f/\partial n = \ln (N/n - 1) + \left(2Nn - 1\right) N\beta \xi + 2\nu = \ln \left(1/\rho - 1\right)$$

$$+ (2\rho-1) N\beta \xi + 2\nu = 0$$

so that:

$$\rho = \frac{1}{2} \left\{ 1 + \tanh\left(\frac{(\rho-1/2) N\beta \xi + \nu}{2}\right) \right\}$$

(399a)

$$\left(\rho-1/2\right) = \frac{1}{2} \tanh\left(\frac{(\rho-1/2) N\beta \xi + \nu}{2}\right)$$

(399b)

Or

$$2x = \tanh(ax + b)$$

(399c)

where

$$x = (\rho-1/2) ; a = N\beta \xi ; b = \nu$$

(399d)

Equation (399) permits determination of $\rho$ for any given value of the parameter $\nu$. It is apparent from an inspection of equation (399) that the phase transition is a degenerate one when $N\to\infty$, for then $\rho=0$ and $\rho=1$ are the only possible solutions. The isotherms then look

<table>
<thead>
<tr>
<th>N</th>
<th>$T_c$ (computes)</th>
<th>$T_c$ (equ. 396)</th>
<th>$T_c$ (comp.)/$T_c$ (equ. 396)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1233.76</td>
<td>1600</td>
<td>0.78</td>
</tr>
<tr>
<td>100</td>
<td>2637.53</td>
<td>3200</td>
<td>0.82</td>
</tr>
<tr>
<td>200</td>
<td>5558.49</td>
<td>6400</td>
<td>0.87</td>
</tr>
<tr>
<td>240</td>
<td>6729.81</td>
<td>7680</td>
<td>0.88</td>
</tr>
</tbody>
</table>
like the one in Figure 22, since from equation (387b) in that limit:

\[ q_\infty = \rho \ln(1-\rho/\rho) - \ln(1-\rho) - \rho(1-\rho)NBc + 2\rho \zeta = 2\rho \zeta, (\rho = 0 \text{ or } \rho = 1) \]

(400)

The interaction considered in this section represents an interesting limiting case which lies at the other end of the spectrum from the nearest-neighbor approximation considered earlier. It can be thought of either as a one-dimensional system with interaction forces of infinitely long range, or alternatively as an N-dimensional system in which all cells are nearest neighbors. The analysis above shows that such a system is subject to a change of phase at all finite temperatures. The model, furthermore, depicts the transition correctly without recourse to the Maxwell construction.
Chapter VII

ANALYSIS OF FINITE SYSTEMS

In the preceding chapter certain fluid systems were considered for which the partition function could be summed explicitly so that it was possible to investigate the thermodynamic limit, i.e. $N \to \infty$. This is not possible for an arbitrary potential. However, the partition function, equation (178) is well suited to numerical analysis. The present chapter is therefore devoted to a consideration of finite systems for which the thermodynamic properties were determined by high-speed electronic computer. It should be said at the outset that these results are not approximations; they are exact computations based on the complete partition function and are approximations only in the sense that the entire model is an approximation to a real system.

The computer used for this work was an IBM 360, model 40. Despite the high speed of this hardware it proved feasible to analyze systems with less than 16 cells only. Computer time increased very rapidly with increasing system size, and became prohibitive for systems larger than $N=15$. Despite this rather stringent limitation on size, fluid systems based on the present model exhibit many of the features of real fluids and form a convenient medium for testing theories and determining, at least qualitatively, the behavior of classical fluids.

A. Formulation of the Problem for Numerical Analysis

From equation (178) we have for a fluid:
\[ q = \frac{p\varepsilon}{KT} = \frac{1}{N} \ln q_N = v + \frac{1}{N} \ln(2\Gamma) \]  

where (cf. equations (4), (6), (36), and (156)):

\[ T(v, a, \xi) = \sum_{n=0}^{[N/2]} \cosh[(N-2n)v] \exp\{-4n\theta\} t_n(1 - \frac{1}{2} \delta_{n,N/2}) \]  

\[ t_n(\beta, N) = \frac{1}{n!} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \prod_{r=1}^{n} \prod_{s=1}^{n} X(q_r - q_s) \, n \neq 0 \]  

\[ t_0 = 1 \]

\[ X_s = \exp(8\theta_s) = \exp\{-\frac{1}{T} (V_s/k + V_{N-s}/k)\} \]

\[ v_s = -\zeta/s \gamma \]

\[ \theta = \sum_{r=1}^{N} \theta_r = \frac{1}{4} \frac{N}{n} V_r \]

The density of the system is then given by (cf. equations (56) and (309)):

\[ \rho = 1/2 (\partial q/\partial v)_\beta = 1/2 (1 + T_\beta/NT) \]  

where:

\[ T_v = (\partial T/\partial v)_\beta = \sum_{n=0}^{[N/2]} (N-2n) \sinh[(N-2n)v] \exp\{-4n\theta\} \]

\[ \cdot t_n(1 - \frac{1}{2} \delta_{n,N/2}) \]  

Using equation (310) one obtains for the compressibility:

\[ K_T = (\beta\varepsilon/2\rho^2)(\partial \rho/\partial v)_\beta = (\beta\varepsilon/4\rho^2)[T_{v_\beta}/NT - \frac{1}{N} (T_\beta/T)^2] \]

\[ = (\beta\varepsilon/4\rho^2)[T_{v_\beta}/NT - (2\rho - 1)^2 N] \]

where:

\[ T_{vv} = (\partial^2 T/\partial v^2)_\beta = \sum_{n=0}^{[N/2]} (N-2n)^2 \cosh[(N-2n)v] \]

\[ \cdot \exp\{-4n\theta\} t_n(1 - \frac{1}{2} \delta_{n,N/2}) \]
The internal energy density of the system is (cf. equation (313)):

\[ u = - \left( \frac{\partial q}{\partial \beta} \right)_\beta \frac{\xi}{\xi} = - \left[ (\partial q / \partial \nu)_\beta (\partial \nu / \partial \beta) \frac{\xi}{\xi} + (\partial q / \partial \beta) \frac{\nu}{\nu} \right] \]

\[ = \frac{1}{2} \rho k T + \rho \sum_{r=1}^{N} V_r - T_{\beta / N T} \]

where

\[ T_\beta = (\partial q / \partial \beta)_\nu = \sum_{n=0}^{[N/2]} \cosh[(N-2n)\nu]\exp{-4n\theta} \]

\[ \cdot \left[ t_n \sum_{r=1}^{N} V_r + (t_n)_\beta (1 - \frac{1}{2} \delta_n, N/2) \right] \]

\[ (t_n)_\beta = - \frac{1}{n!} \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \sum_{r=1}^{n} \sum_{s=1}^{n} V(q_r-q_s) + V(N-q_r+q_s) \]

\[ \cdot \prod_{k=1}^{n} \prod_{\ell=1}^{n} \chi(q_k-q_\ell) = (\partial t_n / \partial \beta)_\nu \]

\[ \sum_{(r<s)} \]

For the specific heat we have, using equation (324):

\[ C_V = -k \beta^2 \left[ (\partial u_1 / \partial \beta)_\rho + (\partial u_2 / \partial \nu)_\beta (\partial \nu / \partial \beta)_\rho + (\partial u_2 / \partial \beta)_\nu \right] \]

where \( u_1 \) comprises the terms involving \( \rho \), while \( u_2 \) is the last term in (407). For the various partial derivatives required one finds:

\[ (\partial u_1 / \partial \beta)_\rho = - (\rho / 2 \beta^2) \]

\[ (\partial u_2 / \partial \nu)_\beta = (T_\beta T_{\nu / N T^2} - (T_\beta T_{\nu / N T}) = (2\rho - 1)(T_\beta / T - T_{\beta \nu / N T}) \]

\[ T_{\beta \nu} = (\partial^2 q / \partial \beta \partial \nu) = \sum_{n=0}^{[N/2]} (N-2n) \sinh [(N-2n)\nu] \]

\[ \cdot \exp{-4n\theta} [t_n \sum_{r=1}^{N} V_r + (t_n)_\beta (1 - \frac{1}{2} \delta_n, N/2)] \]

\[ (\partial u_2 / \partial \beta)_\nu = (1/N)(T_\beta / T)^2 - (T_{\beta \beta / N T}) \]

\[ T_{\beta \beta} = (\partial^2 q / \partial \beta^2) = \sum_{n=0}^{[N/2]} \cosh[(N-2n)\nu]\exp{-4n\theta} \]

\[ \cdot \left[ (t_n)_\beta \sum_{r=1}^{N} V_r + (t_n)_\beta (1 - \frac{1}{2} \delta_n, N/2) \right] \]}
\[(t_n)_{\beta \beta} = \left( \frac{\partial^2 t_n}{\partial \beta^2} \right)_{\nu} = \frac{1}{n!} \sum_{q_1=1}^{N} \sum_{q_n=1}^{N} \sum_{r_1=1}^{n} \sum_{r_2=1}^{n} \sum_{s_1=1}^{n} \sum_{s_2=1}^{n} (r_1 < s_1) (r_2 < s_2) \]

\[\cdot (V_{q_{r_1}} - q_{s_1}) + V_{N-q_{r_1}} + q_{s_1} (V_{q_{r_2}} - q_{s_2}) + V_{N-q_{r_2}} + q_{s_2} \]

\[
\cdot \prod_{r_3=1}^{n} \prod_{s_3=1}^{n} x (q_{r_3} - q_{s_3}) (r_3 < s_3)
\]

(410f)

From equation (403) we have:

\[(2\rho - 1) N T = T_{\nu} \]

Therefore:

\[(2\rho - 1) N \left[ T_{\nu} (\partial \nu / \partial \beta)_{\rho} + T_{\beta} \right] = T_{\nu\nu} (\partial \nu / \partial \beta)_{\rho} + T_{\nu\beta} \]

so that:

\[
(\partial \nu / \partial \beta)_{\rho} = \left( \frac{T_{\nu\beta} - (2\rho - 1) N T_{\beta}}{(2\rho - 1) N T_{\nu} - T_{\nu\nu}} \right) = \left( \frac{T_{\nu\beta} - (2\rho - 1) N T_{\beta}}{(2\rho - 1)^2 N^2 T - T_{\nu\nu}} \right)
\]

(410g)

Combining these results, the specific heat of the system is found to be:

\[C_{\nu} = \frac{1}{2} k_{\beta} + k_{\beta}^2 \left[ (T_{\beta \beta}/N T) - (1/N)(T_{\beta}/T) \right] \]

\[+ k_{\beta}^2 \left[ (T_{\beta \beta}) - (2\rho - 1) N T_{\beta} \right]^2 / [N T (2\rho - 1)^2 N^2 T - T_{\nu\nu}] \]

(409b)

We wish next to find an expression for the pair correlation function that is amenable to numerical analysis. For this purpose we define an average correlation parameter as follows:

\[S_i = 1/N < \sum_{r=1}^{N} \sigma_r \sigma_{r+i} > \]

(411)

We observe that \(S_i = 1\) if all cells in the system separated by \(i\) cell parameters are either occupied or empty. There is then perfect correlation between these cells. If now one of the cells is occupied while the other is empty for every pair of such cells, then \(S_i = -1\).
This corresponds to perfect anticorrelation. Finally, if among all such cell pairs as many are correlated as are anticorrelated, then $S_i=0$, so that this value of the coefficient corresponds to lack of any correlation (for a density of $\rho=1/2$).

In order to find the relationship between the pair correlation parameters and the usual pair correlation functions it is necessary to express the probability that two cells separated by $i$ cell parameters are occupied in terms of these coefficients. The a priori probability that a given cell is occupied (or empty) is, of course, the same as the a priori probability that a given cell have its occupation index equal to $\pm 1$. Call this probability $W(\sigma_i)$. If there are $<n>$ particles in the system, the probability that a particle is in a given cell is

$$W(\sigma_i) = \frac{<n>}{N} = \rho$$

(412)

The joint probability that cell $i$ and $j$ be occupied is:

$$W(\sigma_i, \sigma_j) = W(\sigma_i/\sigma_j)W(\sigma_j) = \rho W(\sigma_i/\sigma_j)$$

(413a)

where $W(\sigma_i/\sigma_j)$ is the conditional probability that cell $j$ have occupation index $\sigma_j$, given that cell $i$ has occupation index $\sigma_i$. Let the conditional probability be defined in terms of a coefficient $C_{ij}$ as follows:

$$W(\sigma_i/\sigma_j) = W(\sigma_j) (1 + C_{ij}) = \rho (1 + C_{ij})$$

(413b)

so that:

$$W(\sigma_i, \sigma_j) = W(\sigma_i) W(\sigma_j) (1 + C_{ij}) = \rho^2 (1 + C_{ij})$$

(413c)

From equation (413b) we read that the probability of cell $j$ having the same occupation index as cell $i$ is $\rho(1 + C_{ij})$. Now, the probability of cell $j$ having the same occupation index as cell $i$ and the probability of its having the opposite occupation index are
mutually exclusive events. Hence the latter probability is 1-\rho(1+C_{ij})=(1-\rho)-\rho C_{ij}. Then the average value \langle \sigma_i \sigma_j \rangle can be determined as follows:

\[ \langle \sigma_i \sigma_j \rangle = (\text{probability that cells } i \text{ and } j \text{ have the same occupation index})(+1) + (\text{probability that cells } i \text{ and } j \text{ have opposite occupation indices})(-1) \]

\[ = \rho(1+C_{ij}) + (-1)[(1-\rho)-\rho C_{ij}] \]

\[ = 2\rho(1 + C_{ij})-1 \]

Or

\[ 1 + C_{ij} = (1/2\rho) \left(1 + \langle \sigma_i \sigma_j \rangle\right) \]

Consequently, using equations (413c) and (414), we find that

\[ W(\sigma_i, \sigma_j) = \rho^2(1 + C_{ij}) = \rho/2 \left(1 + \langle \sigma_i \sigma_j \rangle\right) \]  

(415)

From which one concludes, using equation (411) that:

\[ S_i = 1/N < \sum_{r=1}^{N} \sigma_r \sigma_{r+i} > = (2/N\rho) \sum_{r=1}^{N} W(\sigma_r, \sigma_{r+i}) - 1 \]

(416a)

It is readily verified that this relation gives the correct limiting values for \( S_i \) commented on above: if there is no correlation, then \( W(\sigma_r, \sigma_{r+i})=\rho^2 \), so that if there is no correlation:

\[ S_i = (2\rho-1) \]

(416b)

\[ = 0 \quad \quad \quad \quad \quad (\rho=1/2) \]

If the correlation is perfect, then \( W(\sigma_r, \sigma_{r+i})=\rho \), so that for perfect correlation:

\[ S_i = +1 \]

(416c)

Finally, if there is perfect anticorrelation, then \( W(\sigma_r, \sigma_{r+i})=0 \), so that

\[ S_i = -1 \]

(416d)

The usual pair correlation function (cf. Hill, ref. 3, equations (29,20)) is defined in terms of the present model as:
\[ W(\sigma_i, \sigma_j) = W(\sigma_i)W(\sigma_j)C(\sigma_i, \sigma_j) = \rho^2C(\sigma_i, \sigma_j) \]  

Combining equations (416a) and (417) we have that:

\[ S_i = \frac{1}{N} < \sum_{r=1}^{N} \sigma_r \sigma_{r+i} > = \frac{2\rho}{N} \sum_{r=1}^{N} C(\sigma_r, \sigma_{r+i}) - 1 \]

In terms of the Kirkwood correlation functions, which are more commonly used in connection with fluids, we have the following relationship:

\[ S_i = (2\rho/N)(N/N-1) \sum_{r=1}^{N} g^2(\sigma_r, \sigma_{r+i}) - 1 \]

\[ = (2\rho/N-1) \sum_{r=1}^{N} g^2(\sigma_r, \sigma_{r+i}) - 1 \]

If one adopts the point of view generally taken in dealing with fluids, that the correlation functions can depend only on the separation of the two cells and not on the location of these cells, i.e. that all cells in a fluid are equivalent, then each term in the sum (419) will yield the same result. We can therefore write:

\[ S_i = \frac{1}{N} \sum_{r=1}^{N} <\sigma_r \sigma_{r+i}> = <\sigma_o \sigma_{o+i}> \]

\[ = [2\rho/(1-\eta)]g^2(x_i) - 1 \]

where \( x_i = (i\lambda), \lambda \) being the cell parameter. Here \( g(x) \) is the usual radial distribution function. As a convenient check that this is the correct relation, we observe that:

\[ \sum_{i=1}^{N} S_i = \sum_{i=1}^{N} <\sigma_o \sigma_{o+i}> = \sum_{i=1}^{N} \sigma_i > (\sigma_o) = (2\rho-1)N \]

\[ = (2\rho N/N-1) \sum_{i=1}^{N} g^2(x_i) - N = (2\rho-1)N \]

where equation (29.31) in Hill\(^3\) and equation (49) above were used. We may also observe that \( S_i = \sigma_i \), where \( \sigma_i \) is the short-range order parameter defined previously by equation (314).
Having now established the connection between the \( S_i \)'s and the correlation functions as usually defined, we shall refer to the former simply as "correlation functions" from now on.

The correlation functions can be computed from the partition function (cf. equations (35) and (37)) as follows:

\[
(\partial/\partial \theta_i \ln z_N) = 2 \sum_{\{\sigma\}} \left\{ \left( \sum_{k=1}^N \sigma_k \sigma_{k+1} \right) \exp \left\{ \sum_{r=1}^N \sum_{s=1}^N \sigma_r \sigma_{r+s} \theta_s \right\} \cdot \exp \left\{ \nu \sum_{r=1}^N \sigma_r \right\} \right\}
\]

The factor 2 comes from the fact that \( \theta_i = \theta_{N-i}^* \). Therefore:

\[
S_i = \frac{1}{2} (\partial/\partial \theta_i) \left( \frac{1}{N} \ln z_N \right) = (1/2N)(\partial/\partial \theta_i) \left[ \ln (C_N^{-1} Q_N) \right]
\]

\[
= (1/2N)(\partial/\partial \theta_i) \left[ \ln (\exp (N\theta) T) \right]
\]

\( C_N \) being defined by equation (37) and \( T \) by (402a). Thus one finds that

\[
S_i = 1 + (T_{\theta_i} / 2NT)
\]

where:

\[
T_{\theta_i} = (\partial T/\partial \theta_i) = \sum_{n=1}^{[N/2]} \cosh[(N-2n)\nu] \exp(-4n\theta)[(t_n')_{\theta_i} - 8nt_n]
\]

\[
(1 - \frac{1}{2} \delta_{n,N/2})
\]

\[
(t_n')_{\theta_i} = (\partial t_n/\partial \theta_i) = 8 \sum_{q_1=1}^{N} \cdots \sum_{q_n=1}^{N} \sum_{r=1}^{N} \sum_{s=1}^{N} (\partial/\partial \theta_i)(\theta_q - q_s)
\]

\[
(\nu > 0) \quad (r<s)
\]

The relationship can readily be checked in some limiting cases. Thus for \( \theta_i = \infty \), i.e. \( V_i = -\infty \), \( T_n = 0 \) for \( n \neq 0 \) (cf. the discussion in

*It is assumed for simplicity that \( N \) is odd.*
Chapter V, Section A), so that \( T_{\theta_i} = \frac{\partial}{\partial \theta_i} \left[ \cosh(N\nu) \right] = 0 \). Consequently, \( S_1 = 1 \) in this case, so that there is perfect correlation. The infinitely strong attractive potential has effectively caused the two cells to merge into one. Some care is necessary in establishing the value of \( S_0 \). Observing that \( V_0 = \infty \), i.e. \( \theta_0 = -\infty \), one would expect that two cells connected by such a potential become separate and disjoint entities with perfect anticorrelation between them, i.e. \( S_i = -1 \). This conclusion being independent of the index \( i \) holds for \( S_0 \) as well. This is another facet of the exclusion principle that has been built into the model. This same conclusion can be reached by observing that \( t_n \) is not a function of \( \theta_0 \) in view of the primed summation. Hence \( (t_n)\theta_0 = 0 \) so that

\[
T_{\theta_0} = -8 \sum_{n=1}^{[N/2]} n \cosh[(N-2n)\nu] \exp(-4\theta)t_n \left( 1 - \frac{1}{2} \delta_{n,N/2} \right)
\]

In the limit as \( \theta_0 \to -\infty \), the dominant term in the sum is \( n = N/2 \) so that \( (T_{\theta_0}/2NT) = -2 \), which then also leads to \( S_0 = -1 \).

The various thermodynamic functions of systems with up to 15 cells were computed by means of the program at Appendix VIII. The results are presented and analyzed in the next section.

B. Presentation and Analysis of Computer Data for Finite Systems

1. One-Dimensional Systems

Specific heat curves for systems ranging in size from two to fourteen cells were computed for various interaction potentials from the program at Appendix VIII. Figure 30 shows the resulting curves for an interaction potential having a depth parameter \( \zeta = 64 \) and a range parameter \( \gamma = 6 \) (cf. equation (402d)). Not all curves
SPECIFIC HEAT V.S. DENSITY
ONE-DIMENSIONAL SYSTEM
\( Y = 64 \text{ K} \), \( Y = 6 \), \( p = \frac{3}{2} \)

FIG. 30
are shown in order not to make the graph confusing. The specific heat curves exhibit a clear maximum which becomes steeper with increasing system size and moves toward lower temperatures. The following table summarizes this information:

<table>
<thead>
<tr>
<th>N</th>
<th>(T_c) (°k)</th>
<th>(\zeta/\text{k}T_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>26.68</td>
<td>2.395</td>
</tr>
<tr>
<td>4</td>
<td>20.90</td>
<td>3.060</td>
</tr>
<tr>
<td>6</td>
<td>17.99</td>
<td>3.560</td>
</tr>
<tr>
<td>9</td>
<td>15.64</td>
<td>4.090</td>
</tr>
<tr>
<td>10</td>
<td>15.14</td>
<td>4.220</td>
</tr>
<tr>
<td>11</td>
<td>14.74</td>
<td>4.340</td>
</tr>
<tr>
<td>12</td>
<td>14.33</td>
<td>4.440</td>
</tr>
<tr>
<td>13</td>
<td>14.08</td>
<td>4.550</td>
</tr>
<tr>
<td>14</td>
<td>13.76</td>
<td>4.650</td>
</tr>
</tbody>
</table>

It is apparent from the graph and the table that the maxima approach a limit. The sequence of maxima seems to be a nonincreasing one, bounded of course from below. However, the limited number of systems on which data could be calculated does not allow determination of this limit with any degree of certainty. If one attempts to expand \(\zeta/\text{k}T_c\) in inverse powers of \(N\) thus:

\[
\frac{\zeta}{\text{k}T_c} = a + \frac{b}{N} + \frac{c}{N^2}
\]

and fits the parameters \(a\), \(b\), and \(c\) to the above data, one finds that:

\[
\frac{\zeta}{\text{k}T_c} = 6.43 - \frac{31.16}{N} + \frac{87.36}{N^2}
\]
The following table gives a comparison of the values obtained from this formula with the true ones:

**TABLE 7**

<table>
<thead>
<tr>
<th>N</th>
<th>True</th>
<th>$\xi/\kappa T_C$</th>
<th>Equ. (146)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>4.65</td>
<td>4.65</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>4.55</td>
<td>4.55</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>4.44</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>4.34</td>
<td>4.32</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4.22</td>
<td>4.18</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4.09</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.56</td>
<td>3.66</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.06</td>
<td>4.10</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.39</td>
<td>12.69</td>
<td></td>
</tr>
</tbody>
</table>

It is seen that the fit is excellent for systems of six or more cells, but is not reliable for very small systems. If equation (424) were to remain approximately correct for large systems, one would conclude that:

\[
\lim_{N \to \infty} \frac{\xi}{\kappa T_C} = 6.43 \tag{425a}
\]

Or:

\[
\lim_{N \to \infty} T_C \sim \frac{\xi}{\kappa} / 6.43 = 64/6.43 \sim 10^6 k \tag{425b}
\]

where the Neon or Helium-like potential with $\xi=64k$, ($\gamma=6$) was used on which Fig. 30 is based. While the temperature is of about the right order of magnitude, one cannot be sure, of course, that equation (416) will continue to hold for large systems. One can also not say with
any certainty whether the system will undergo a phase transition in
the thermodynamic limit \( (N\rightarrow\infty) \). Although the specific heat curve
maxima become higher and steeper with increasing system size, it is
not clear whether the specific heat curve will actually have a
singularity in the limit \( N\rightarrow\infty \). The analysis in Chapter VII,
where the corresponding system was discussed in the limit \( \gamma\rightarrow0 \),
suggests that this will be the case.

Figure 31 affords a comparison between the specific heat curve
of the same system, \( N=12 \), for different interaction potentials. It
will be observed that the maximum of the curve corresponding to the
deeper potential will occur at a higher temperature and is somewhat
broader than that of the curve corresponding to the lower potential.
The curves are in excellent agreement with equation (424), inasmuch
as the extremum of the curve corresponding to \( \gamma=128k \) occurs at very
nearly twice the temperature of the maximum of the \( \zeta/k=64 \) curve.
In view of the broadness of the maxima, this result is certainly well
within the accuracy of the data.

Specific heat curves for various range parameters and depths
for a system of ten cells are compared in Figure 32. Figure 32A
displays curves for a Neon-like interparticle potential, \( \gamma=64k \),
while in Figure 32B similar curves are plotted for an Argon-like
potential of \( \gamma=512k \). One again observes that a deeper potential
well shifts the maxima of the specific heat curves to higher
temperatures. The graphs also show once more that equation (424)
is obeyed within the range of accuracy of the data. The effect
of increasing the effective range of the interaction, i.e. of decreasing
the parameter \( \gamma \), is apparently similar to that of increasing the depth
SPECIFIC HEAT VS. TEMPERATURE
ONE-DIMENSIONAL SYSTEM

$N = 10 \quad \varphi = 64 K \quad \rho = \frac{1}{2}$

Figure 32A
of the potential well in that the maxima of the specific heat curves are shifted to higher temperatures. In addition, the height of the maxima increases gradually with increasing range of the potential. The following table summarizes the relationship between temperature and range obtained from the graphs:

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$\xi=64k$</th>
<th>$\xi/KT_c$</th>
<th>$\xi=512k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>4.22</td>
<td>4.50</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.12</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.14</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.05</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.33</td>
<td>----</td>
<td></td>
</tr>
</tbody>
</table>

One can incorporate the $\gamma$ and $\xi$ dependence into equation (424) by a slight modification:

$$(\xi/KT_c) = \alpha_\gamma \exp\{ (m-1)/100 \} \left( 1.53 - \frac{7.42}{N} + \frac{20.80}{N^2} \right)$$

where $m$ is given by:

$$\xi = 2^m k$$

and

$$\alpha_\gamma = \gamma - (\gamma-1)(\gamma-2)(\gamma-3)/(18 + 2\gamma)$$

This equation fits the computed data with quite good accuracy.

The compressibility of systems of various sizes is plotted versus temperature in Figure 33. The behavior exhibited in these plots accords with what one would expect on physical grounds: high compressibility at low temperatures when thermal activity is small, and decreasing
COMPRESSION VS. TEMP.
ONE-DIMENSIONAL SYSTEM

\[ \frac{1}{\gamma} = 64K \quad \gamma = 6 \quad \rho = \frac{1}{2} \]
compressibility with increasing temperature because of the increased thermal activity of the particles which make reductions in volume more costly energetically. The increase in compressibility with increasing size of the system also is in keeping with physical intuition; i.e. the attractive interaction becomes more effective with increasing system size. For a given density and temperature, this results in a reduction of the pressure as the size of the system is increased (see below), and this in turn makes it less costly energetically to reduce the volume of the system.

In Figure 34 the compressibility versus temperature curves for interactions of varying ranges are compared. All curves are for a system of ten cells. It is seen that compressibility increases with range, as one would expect. The interaction becomes more effective as the range is increased, thus reducing the pressure; this makes it easier, energetically, to reduce the volume of the system. Hence compressibility is increased. No anomalous behavior is evident in the compressibility curves, nor would one expect to find any such behavior in a plot of compressibility versus temperature.

Pressure-temperature data are graphed in Figure 35 and 36. Figure 35 compares systems of varying size, while Figure 36 shows the effect on pressure of changing the range of the potential. It is seen that the pressure decreases as the size of the system increases or as the potential range is increased.

Pressure-density curves for systems of various sizes are shown in Figure 37. One observes that the curves exhibit the behavior expected of a fluid, but show no evidence of any phase transition. As the system size increases the pressure is reduced substantially and the
COMPRESSIBILITY VS. TEMPERATURE

$N = 10$

1-DIM. SYSTEM

$y = 64 K_j, \quad \rho = \frac{1}{2}$

$\gamma = 0$

$\gamma = 1$

$\gamma = 2$

$\gamma = 3$

$\gamma = 6$

FIG. 34

Temperature vs. compressibility for a 1-DIM. system with $N = 10$, $y = 64 K_j$, and $\rho = \frac{1}{2}$, showing different curves for various $\gamma$ values.
PRESSURE VS. TEMPERATURE
ONE-DIMENSIONAL SYSTEM

\[ \gamma = 64 \text{K}; \rho = \frac{1}{2} \]
N=10
1-DIM. SYSTEM

\[ y = 64k; \cdot \rho = \frac{1}{2} \]

FIG. 36
PRESSURE VS. DENSITY
ONE-DIMENSIONAL SYSTEM
\[ \beta = 6.4 \text{ K} \quad \gamma = 6 \]
\[ T = 10^\circ \text{ K} \]

N = 12
N = 9
N = 6
N = 4
N = 2

FIG. 37
isotherm flattens out. The pressure-density isotherms for a system of 12 cells in Figure 38 also exhibit normal fluid behavior, but no evidence of any phase transition below the "critical" temperature of 14.33°k. There is, however, a noticeable flattening of the pressure-density curve below that temperature that is somewhat reminiscent of the behavior in Figure 26 of the \( N=20 \) subcritical system. This characteristic behavior is brought out more clearly by Figure 39, which shows the "critical" isotherms for a system of ten cells with various interaction potentials. Two potential well depths, 64k and 512k, are considered with range parameters from zero to six. These are the same potentials and ranges for which the specific heat curves are shown in Figure 32. The plot shows once more the marked flattening of the pressure-density curve and the characteristic inflection, which could presage a phase transition as the size of the system is increased. It is found interestingly enough that all critical isotherms fall inside the narrow band bordered by the two curves marked A and B in Figure 39. In fact, most of the isotherms coincide with the upper curve to a very good approximation. As the size of the system increases it appears likely that all of the curves will actually merge into a single one. This behavior suggests that the law of corresponding states applies approximately to the system under consideration. One surmises that it will probably hold exactly in the thermodynamic limit.\(^2\)\(^3\) At the critical density, \( \rho_c=1/2 \), we find from the upper curve, which coincides with all but two of the isotherms, that \( p_c/\rho TC_c = 0.135 \). Consequently:

\[
\beta_c p_c V_c = \beta_c p_c \ell/\rho_c = 0.270
\]
PRESURE VS. DENSITY
ONE-DIMENSIONAL SYSTEM
γ = 6 + K  γ = 6
N = 12

\[ \frac{P \ell}{kT} \]

\[ T = 30° \]
\[ T = 20° \]
\[ T = 14.33° \]
\[ T = 5° \]

FIG. 38
PRESSURE VS. DENSITY
ONE-DIMENSIONAL SYSTEM

N = 10

CRITICAL ISOTHERM A
\( Y = 64 \times 10^3 \); \( Y = 0, 1, 2, 3, 6 \)
\( Y = 512 \times 10^3 \); \( Y = 1 \)

CRITICAL ISOTHERM B
\( Y = 512 \times 10^3 \); \( Y = 3, 6 \)

FOR \( T \) SEE FIG. 32A & B

FIG. 39
Hill shows in Table II, p. 232, that the mean value of this parameter for Ne, N₂, A, and CH₄ is 0.292. The potentials giving rise to the isotherms in Figure 39 are approximately those for Neon (ζ=64k) and Argon (ζ=512k). The value of this parameter determined for a finite system of rather modest dimensions from the partition function, equation (178), thus lies within 7.5% of the average experimentally observed value for three-dimensional systems with similar interaction potentials.

Figure 40 shows compressibility versus density curves for systems of various sizes, all at the subcritical temperature of 10°k. The behavior exhibited is typical for fluids not undergoing a phase transition. No anomalies are observed. As previously noted, the increased effectiveness of the interaction potential in larger systems causes the compressibility to increase as the size of the system is increased. The compressibility-versus-density curves of a ten-cell system at the critical temperatures are plotted to a much larger scale in Figure 41. The curves correspond to various ranges of the interaction potential, all for a Neon-like well depth (ζ=64k). They are the counterpart of the p-ρ curves in Figure 39. Two of the curves corresponding to very long-range potentials are beginning to show anomalies that quite possibly presage a local maximum in the compressibility curve indicative of a phase transition. The corresponding, more fully developed behavior of a much larger system was portrayed in Figure 27. Examining Figure 39 once more it is apparent that this part of the compressibility curve corresponds to the slight but noticeable inflection in the p-ρ curves at low densities.
COMPRESSIBILITY VS. DENSITY
ONE-DIMENSIONAL SYSTEM
\( \gamma = 64 \) \( K \)
\( n = 6 \)
\( T = 10^\circ K \)

FIG. 40
Figure 41

One-Dimensional System

- $Y = 6; T_e = 15.14^\circ K$
- $Y = 3; T_e = 20.48^\circ K$
- $Y = 2; T_e = 29.84^\circ K$
- $Y = 1; T_e = 60.10^\circ K$
- $Y = 0; T_e = 193.95^\circ K$

Compressibility vs. Density

$\gamma = 64 K$

$N = 10$
One expects that these anomalies will become increasingly more pronounced in systems of larger size. Since increase in system size and extension of the potential range are somewhat equivalent ways of increasing the effectiveness of an interaction potential, it is likely that such anomalies will also begin to appear in larger systems for potentials of shorter range. Indeed, Figures 43C and D are computer plots of the pressure and compressibility curves of a system of 12 cells with a Neon-like interaction potential. One sees in Figure 43D the beginning of just such an anomaly in the compressibility curve at the critical temperature for a shorter range potential ($\gamma=6$).

Figure 42 shows the variation of the heat capacity at constant volume with density. Since the curves reflect the change of the heat capacity per cell, i.e. of the specific heat, with changes in density it is clear that the heat capacity should increase as the density increases. In order to verify the behavior at high densities, one has from thermodynamics that:

$$ds = \frac{1}{T} \left( \frac{\partial u}{\partial T} \right)_v \, dT + \frac{1}{T} \left[ \left( \frac{\partial u}{\partial \nu} \right)_T + p \right] d\nu$$

so that

$$\left( \frac{\partial u}{\partial \nu} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p$$

And since:

$$du = \left( \frac{\partial u}{\partial T} \right)_v \, dT + \left( \frac{\partial u}{\partial \nu} \right)_T \, d\nu = C_v \, dT + \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] d\nu$$

one finds (since $du$ is a perfect differential) that:

$$\left( \frac{\partial C_v}{\partial \nu} \right)_T = \left( \frac{\partial^2 u}{\partial \nu^2} \right)_T = T \left( \frac{\partial^2 p}{\partial T^2} \right)_v = T \left( \frac{\partial^2 p}{\partial T^2} \right)_p$$

Or

$$\left( \frac{\partial C_v}{\partial \rho} \right)_T = -\left( \frac{\partial T}{\partial \rho^2} \right) \left( \frac{\partial^2 p}{\partial T^2} \right)_p$$

(418)

Since $p \rightarrow \infty$ as $\rho \rightarrow 1$ for all $T>0$, we have that $\left( \frac{\partial^2 p}{\partial T^2} \right)_p=1=0$, and
SPECIFIC HEAT VS. DENSITY
ONE-DIMENSIONAL SYSTEM

\( \gamma = 64 \text{K} \); \( \gamma = 6 \)

\( T = 10^6 \text{K} \)

\[ \begin{align*}
N &= 12 \\
N &= 11 \\
N &= 9 \\
N &= 6
\end{align*} \]

FIG. 42
SPECIFIC HEAT
VS.
TEMPERATURE

N=14
1-DIM.
SYSTEM
y=64k; \gamma=6

FIG. 43A
PRESSURE VS. DENSITY
ONE-DIMENSIONAL SYSTEM
\( Y = 64 K \); \( Y = 6 \)

\( N = 14 \)

\( T = 13.76^\circ K \)
N=12
1-DIM. SYSTEM
TEMP=14.33 K
\( y = 64 \text{ K} \)

PRESURE VS. DENSITY
COMPRESSIBILITY
VS
DENSITY

N=12
1-DIM.
SYSTEM
T=14.33
Y = 64 K

FIG. 43 D
hence \( \lim_{\rho \to 1} (\partial C_v / \partial \rho)_T = 0 \). This behavior is clearly reflected in the graph.

To complete the discussion of one-dimensional systems, the specific heat versus temperature curve and \( p-\rho \) curve for the largest system analyzed, \( N=14 \), are shown in Figures 43A and B. The specific heat curve shows the very pronounced maximum discussed previously, while the \( p-\rho \) curve exhibits the characteristic inflection at low densities that was observed and discussed in Figures 39 and 43C.

The pair correlation functions of one-dimensional systems are examined in Figures 44 through 48. Typical pair correlation functions for a given temperature and potential are plotted in Figure 44 for typical systems ranging in size from 5 to 15 cells. These are seen to agree quite well qualitatively with experimental curves and curves for radial distribution functions computed theoretically by other methods.\(^3\)\(^8\)\(^9\) Thus, in the hard-core repulsive region perfect anticorrelation prevails. Just outside the hard-core region, the correlation curves rise to a peak, which in the larger systems is quite pronounced and steep, indicating that a high degree of correlation prevails there. The curves then tail off and approach zero asymptotically, indicating no correlation at larger distances for \( \rho = 1/2 \).

There is one difference, however, in these curves and those obtained by other methods. There is a complete absence of any of the local maxima and minima that are usually so characteristic of these curves and which are normally considered as remnants in the liquid state of the first neighbor, second neighbor, etc. shells surrounding a given particle at an equilibrium lattice position.\(^3\) The curves obtained from the present model are seen to be non-increasing discrete functions.
PAIR CORRELATION FUNCTIONS
ONE-DIMENSIONAL SYSTEM

\[ \rho = 0.4 \, \text{K} ; \quad \nu = 6 \]

\[ T = 32^\circ \, \text{K} \]

\[ \rho = \frac{1}{2} \]

FIG. 44A
PAIR CORRELATION FUNCTIONS
ONE-DIMENSIONAL SYSTEM
\[ y = 64K \; ; \; \gamma = 6 \]
\[ T = 32^\circ K \]
\[ \rho = \frac{1}{2} \]

**FIG. 44B**
This difference in behavior appears to be due to the discrete cellular space grid which is such an essential part of the present model.

De Boer has shown that the undulating behavior is due to contributions to the potential of average force from the screening effect of particles surrounding the particle of interest. This is the same effect which in the hard sphere model results in a pseudo-attractive force. The effect, according to de Boer, is to superpose an extra repulsive force at distances smaller than 1.5\(\ell\) and an extra attractive force between 1.5\(\ell\) and 2.2\(\ell\), and a small repulsive force for larger distances.

In the present model, all potentials are averaged over the whole cell. Thus, the variations discussed by de Boer are smeared out over the entire cell and are more than compensated for by the attractive true Lennard-Jones potential.

Before leaving Figure 44, it is worthwhile noticing that even at great distances, relatively speaking, the correlation is nonzero. This is, of course, due to the Lennard-Jones potential used here which, even for \(\gamma = 6\), has an infinite range. This will clearly still hold true in systems of very large size, the correlation going to zero only as the separation distance becomes infinite.

In Figure 45 we see the effect of temperature on the correlation functions of a system of 13 cells. At temperatures well below the critical point one sees that correlation is perfect, or very nearly so, throughout the entire system. All cells are nearest neighbors, as it were. If one cell is occupied there is thus a very high probability that all cells are occupied. That is to say, long-range order exists. As the temperature increases, correlation is reduced somewhat in cells far removed from the cell of interest, but correlation is still
PAIR CORRELATION FCTS.
ONE-DIMENSIONAL SYSTEM

\[ N = 13, \ y = 64K, \ y = 6, \ \rho = \frac{1}{2} \]

\[ T_c = 14.08^\circ K \]

FIG. 45
quite high throughout the system. As the critical point is passed, correlation drops markedly in cells more than two or three cell parameters removed from the one of interest. At temperatures substantially above the critical temperature, correlation is practically non-existent except in neighboring cells or cells that are next-nearest neighbors. That is to say, short-range order has replaced long-range order in the system. There is, then, a very noticeable change in correlation and hence in order as the critical temperature is passed.

This feature is more apparent in Figure 46, which plots the various correlation functions for this same system versus temperature. While $S_1$, the nearest-neighbor correlation or short-range order parameter, decreases only gradually after the critical temperature is passed, the longer range correlations begin to drop off a little before the critical temperature is reached, and then decrease very rapidly and approach zero after that temperature has been passed. The graph shows quite clearly how long-range order changes to short-range order above the critical temperature. This behavior is completely analogous to that found by Kaufman and Onsager in their analysis of the two-dimensional Ising ferromagnet. The point of interest here is that in the ferromagnet this behavior is associated with a change of phase. It is very suggestive that this is happening in the present system also. As we pass from a temperature above $T_c$ through the critical temperature, correlation throughout the system increases markedly. By virtue of this correlation, the tendency is to change the density of the system. To see this, consider a system at density $\rho=1/2$, as it passes $T_c$ from above. Suppose that a
PAIR CORRELATION FUNCTIONS
VS. TEMPERATURE
ONE-DIMENSIONAL SYSTEM
\( y = 64K \); \( \gamma = 6 \); \( \rho = \frac{4}{2} \)
\( N = 13 \)

FIG. 46
temporary fluctuation increases the density of the phase under consideration to \( \rho = 1/2 + \epsilon \) at a temperature \( T < T_c \). The density of the other phase in equilibrium with the one of interest is then \( 1 - \rho = 1/2 - \epsilon = \rho' \). By virtue of the strong correlation that exists throughout the system, there is now a tendency for all cells in phase I to become occupied, since \( 1/2 + \epsilon \) cells already are, while in phase II the majority of cells, i.e. \( 1/2 + \epsilon \), are unoccupied. The tendency is therefore for all cells to be vacated in that phase. If the system is large enough for this tendency to become an avalanche effect, a phase change will in fact occur. This is not the case in the relatively small systems under study here, as was seen in the analysis of the \( p-\rho \) and compressibility curves. However, the correlation functions in Figure 46 make it seem very likely that such a transition will occur in larger systems, particularly when this correlation function behavior is viewed in the light of the other evidence for such a transition in the present system: the anomalies in the compressibility curves, the slight though characteristic inflection of the isotherms below \( T_c \), the evidence of the specific heat curves, and the proved existence of a transition in systems with very long-range interactions (Chapter VII, D).

Figure 47 also is a plot of correlation functions versus temperature, showing the effect on correlation of changing the potential depth and range. As regards the former, one sees that the effect of changing the depth of the attractive potential is merely to change the critical temperature. The configuration of the correlation curves about the critical temperature remains qualitatively the same. Changing the range has a similar effect; the critical temperature is
AVERAGE PAIR CORRELATION FCTS.
DEPENDENCE ON POTENTIAL RANGE
ONE-DIMENSIONAL SYSTEM
$y = 512 K; \phi = \frac{1}{2}$
$N = 10$

FIG. 47
shifted, but the configuration of the correlation curves about $T_c$ is not materially affected. The graphs in the figure are for the same system as the one discussed in connection with Figures 32 and 39.

The variation of correlation with density is graphed in Figure 48. One finds that at $\rho=0$ and $\rho=1$, correlation is perfect. This is obviously so, since for these two states all occupation indices are the same. The correlation curves are symmetric about $\rho=1/2$, varying inversely with the density, i.e. inversely with the number of microstates available for the given macrostate. Since this degeneracy is symmetric about $\rho=1/2$, one would expect the curves to exhibit the same symmetry. The behavior described above is completely in keeping with equation (416) developed above.

2. Two-Dimensional Systems

It is possible to use the program at Appendix VIII to compute the thermodynamic properties of two-dimensional finite systems by defining the potential as in equation (60) above, i.e. by letting

$$V_r = \begin{cases} -5 & (r=1,m) \\ 0 & (r\neq1,m) \end{cases} \quad (\text{mod. } N)$$

Clearly, any system with a total number of cells, $N$, such that $N$ is the product of two prime factors lends itself to conversion to a two-dimensional array. The specific heat curves of typical systems with less than 15 cells total are shown in Figure 49. As in the one-dimensional case, the specific heat curves exhibit a characteristic peak which, in the two-dimensional case, is shifted to considerably higher temperatures. The following table summarizes the
PAIR CORRELATION FUNCTIONS
VS.
DENSITY
\( y = 512 \), \( y = 6 \)
\( T = 113.83 \)
\( N = 10 \)
SPECIFIC HEAT VS. TEMPERATURE
TWO-DIMENSIONAL SYSTEMS

\[ y = 64K ; \quad \theta = \frac{1}{2} \]

\[ N = 14 ; \quad T_c = 35.65 \]
\[ N = 12 ; \quad T_c = 39.34 \]
\[ N = 9 ; \quad T_c = 40.10 \]
\[ N = 8 ; \quad T_c = 39.62 \]
\[ N = 6 ; \quad T_c = 36.76 \]

FIG. 49
information available from computer analysis concerning the critical temperatures of these systems:

<table>
<thead>
<tr>
<th>N</th>
<th>$T_C$</th>
<th>$\zeta/kT_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>36.76</td>
<td>1.74</td>
</tr>
<tr>
<td>8</td>
<td>39.62</td>
<td>1.61</td>
</tr>
<tr>
<td>9</td>
<td>40.10</td>
<td>1.59</td>
</tr>
<tr>
<td>12</td>
<td>39.34</td>
<td>1.62</td>
</tr>
<tr>
<td>14</td>
<td>35.65</td>
<td>1.79</td>
</tr>
</tbody>
</table>

The exact ratio ($\zeta/kT_C$) from Onsager's solution or from symmetry arguments is: \(^{11,16,17}\)

$$\zeta/kT_C = 1.76$$

where the correspondence relations, Table 1, between fluid and magnetic systems were used. It will be seen that the values obtained by numerical methods for small systems fluctuate about the exact ratio, but do not deviate from it by more than about 10%. These fluctuations are attributable to the small size of the systems analyzed and the consequent strong influence of boundary effects. For example, the $N=14$ system consists of seven rows of two particles each (or two rows of seven particles), while the $N=12$ lattice is a relatively symmetric system consisting of three rows of four particles each. The "surface area" for the latter system is therefore substantially less than that of the former. In fact, in the $N=14$ system every particle lies on the boundary, while this is not true of the $N=12$ system.

The compressibility versus temperature and pressure versus
temperature graphs of typical systems are plotted in Figures 50A and B and 51A and B respectively. These curves follow the general pattern of the corresponding one-dimensional ones and no unusual behavior is observed or expected.

Pressure versus density graphs of typical two-dimensional systems are shown in Figure 52. Like the graphs of one-dimensional systems of corresponding size, they exhibit no tendency toward a phase transition other than a slight inflection at low densities and a noticeable decrease in slope around \( p=1/2 \) in the case of the larger systems.

P-\( p \) curves for various temperatures near \( T_c \) are plotted for a system of nine cells in Figure 53 in order to bring out the change in such isotherms with temperature. They show once more the characteristic inflection at low density.

The compressibility versus density curves for the same system are graphed in Figure 54. Like their one-dimensional counterparts (cf. Fig. 41 and 43) they display rather characteristic anomalous behavior at low densities, which coincides with the occurrence of inflections in the p-\( p \) curves. Since we know from the exact solution of the two-dimensional Ising ferromagnet that that system undergoes a phase transition at temperatures below the critical one, it is apparent that this behavior in the small systems analyzed by computer presages a change of phase in larger assemblies. It would consequently be of considerable interest if computer techniques could be developed for coping with substantially larger systems.
N = 9
2-DIM.
SYSTEM

\[ y = 64k^2 \rho = \frac{1}{2} \]
**FIG. 50B**

**COMPRESSION VS. TEMPERATURE**

**N 12**

2-DIM. SYSTEM

\[ y = 64 K \quad \rho = \frac{1}{2} \]
N = 6
2-DIM. SYSTEM

\[ y = 64K \frac{1}{5} = \frac{1}{2} \]
$N=14$

2-DIM. SYSTEM

$y = 64k; p = \frac{1}{2}$

PRESSURE VS. TEMPERATURE

FIG. 51B
2-DIM. SYSTEM

\( y = 64 \text{ K} \)

PRESSURE

VERSUS

DENSITY

\( PV/KT \)

\( N = 14 \)

\( N = 12 \)

\( N = 9 \)

\( N = 8 \)

\( N = 6 \)

\( T = 35.65^\circ \)

\( T = 39.34^\circ \)

\( T = 40.10^\circ \)

\( T = 39.62^\circ \)

\( T = 36.76^\circ \)

FIG. 52
N = 9

2-DIM. SYSTEM

\( \gamma = 64 \, \text{K} \)

FIG. 53
Compressibility vs. Density

$N = 9$

2-DIM.

SYSTEM

$y = 64K$

FIG. 5
3. Three-Dimensional Systems

Just as in the two-dimensional case, it is possible to analyze three-dimensional systems with nearest-neighbor interactions numerically, using the program at Appendix VIII. Only a suitable change in the potential need be made for this purpose. For the analysis that follows the potential of equation (62) was used, with $\zeta=64k$.

Because of the restriction to systems with less than 16 cells, only two three-dimensional arrays are accessible for analysis, i.e. $N=8$, and $N=12$. In the former case, the system is a two-cell cube $(2\times2\times2)$, while the $N=12$ system has a $(2\times2\times3)$ configuration. Their structure is quite similar, and one would not expect these two systems to differ very much. This is found to be the case.

Figure 55 gives the specific heat versus temperature curves for these systems. The critical temperature data are as follows:

<table>
<thead>
<tr>
<th>$N$</th>
<th>$T_c$</th>
<th>$\zeta/kT_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>59.63</td>
<td>1.07</td>
</tr>
<tr>
<td>12</td>
<td>61.32</td>
<td>1.04</td>
</tr>
</tbody>
</table>

No exact solution for the three-dimensional model exists, of course. Generally Wakefield's value for the ratio $\zeta/kT_c$ is considered the most accurate. He obtained

$$\exp\{-2J/kT_c\} = 0.641$$

which, then, gives:

$$2J/kT_c = 0.526$$

But $\zeta=4J$ (cf. Table 1). Hence,

$$(\zeta/kT_c) = 1.05$$
SPECIFIC HEAT VS. TEMPERATURE
THREE-DIMENSIONAL SYSTEMS
NEAREST-NEIGHBOR INTERACTIONS
\( \gamma = 64 \text{K} \); \( \rho = \frac{1}{2} \)

\( T_c = 59.63^\circ \text{K} \) \( 61.32^\circ \text{K} \)

FIG. 55
Other estimates for this ratio range from 0.607, which corresponds to $\xi/kT_c = 1.09$, to 0.717, which corresponds to $\xi/kT_c = 0.98$.\(^8\)

The value obtained from these two models falls well within that range and differs by only 1-2% from the best estimate available today. This is rather remarkable accuracy considering the small size of the systems analyzed. It is no doubt due to the perfect and almost perfect cubic symmetry of these two arrays, so that boundary effects are kept to a minimum. The agreement serves as a further indication of the validity of the model and of the computer analysis. At the same time it confirms other estimates of the critical point.

Compressibility versus temperature and pressure versus temperature graphs for these systems indicate essentially the same behavior as in the one- and two-dimensional case, and are consequently omitted.

P-$\rho$ isotherms for the N=8 system are plotted in Figure 56. They exhibit the characteristic shape but give no indication of any phase change, except for the low-density inflection at sufficiently low temperatures.

Figure 57 is a graph of the critical isotherm for the N=12 system. There is a quite noticeable low-density inflection point which keys in with a corresponding local maximum on the compressibility curve shown in Figure 58. The anomalous behavior of the compressibility curve at low densities and sufficiently low temperature is brought out even more clearly by Figure 59. The figure is a low-density plot of compressibility and of the corresponding pressure for the same system, but at lower temperature, 32°k. This behavior, as noted previously in connection with Figure 26 and the one- and two-dimensional analysis, is probably indicative of an incipient phase transition. No
N = 8

3-DIM. SYSTEM

\( T = 64 \text{ K} \)

FIG. 56
N = 12

3-DIM. SYSTEM

TEMP = 61.32 \degree K

\gamma = 64 K
COMPRESSION VS. DENSITY

4KK+1

0.1 0.2 0.3 0.4 0.5

DENSITY

N=12
3-DIM.
SYSTEM
T=61.32
y=64K

FIG.58
COMPRESSIBILITY VS. DENSITY

PRESSURE VS. DENSITY

THREE-DIMENSIONAL SYSTEM

\[ \gamma = 64 \, \text{K} ; \; T = 32^\circ \text{K} \]

\[ N = 12 \]

FIG. 59
actual transition is apparent in the two small systems analyzed.

C. Summary

The analysis in this chapter demonstrates that the series formulation of the partition function, equation (178), is a versatile tool for determining the thermodynamic properties of fluids and is well suited to evaluation by high-speed electronic computers. Time limitations restricted the analysis to systems of less than 16 cells, however.

While there are a number of indications of incipient phase transitions, no true transition is observed. This is as one would expect; the discussion in Chapter V makes it clear that a true transition can occur only in the thermodynamic limit. This same conclusion emerges also from other arguments based on a theorem of Froebinius dealing with the degeneracy of the maximum eigenvalue of a matrix with all positive coefficients. The investigation in the previous chapter of a fluid with interactions of infinite range ($\gamma=0$) also shows that a phase transition is approached only gradually with increasing system size.

Among the indications of an incipient phase transition are the following:

The specific heat versus temperature plots of all systems analyzed exhibit a well-defined maximum. In the one-dimensional case the maxima appear to approach a limiting critical temperature $T_c = \zeta/6.43k$. For two-dimensional fluids the critical temperature fluctuates about the known exact value of $T_c = \zeta/1.76k$, deviations being within limits of approximately $\pm 10\%$. The fluctuations have their origin in the marked effect of boundary conditions on very small systems, the
boundary conditions in turn being very dependent on the symmetry and size of the system under investigation. Three-dimensional arrays analyzed are quite symmetric. Hence these fluctuations due to boundary effects are not observed and the critical temperature, $T_c = \xi/1.05k$, derived from specific heat data lies within about 1% of the best estimates for three-dimensional Ising systems available today.

Fluids of all dimensions exhibit a small but rather characteristic inflection of the isotherm in a p-p diagram for temperatures below the critical one.

The compressibility versus density plots for these systems show the beginning of anomalous behavior, i.e. the appearance of a small maximum, for temperatures below the critical one and at densities corresponding to those where the inflections remarked on above appear.

Pair correlation functions provide additional evidence suggesting that one-dimensional systems of the type considered here (i.e. systems in which every particle interacts with every other one) are subject to phase transitions. The functions show very clearly that long-range order is present below the critical temperature. But as the temperature is raised above the critical one correlation decreases very rapidly except in neighboring cells so that above the critical temperature only short-range order prevails.

Numerical analysis of finite systems thus demonstrates once more the validity of the model and the versatility of the partition function in the form of equation (178). The analysis also confirms the validity of computing the properties of two and three dimensional systems with a limited number of bonds per particle from a more
general one-dimensional model, as discussed more fully in Chapters II and VI. Finally, the analysis shows that the fluid model adopted in this study leads to realistic thermodynamic behavior which in general agrees at least qualitatively with the known behavior of real fluids.
Chapter IX

CONCLUSIONS

The following conclusions emerge from this study:

The cellular model that underlies the present investigation is capable of giving a realistic, consistent, and versatile account of the thermodynamic behavior of fluids. It is an essential feature of the model, differentiating it from others of its type, that the cells serve merely as a space grid to fix the instantaneous position of the particles. The model is therefore not a lattice gas and incorporates no spurious symmetries that are alien to fluids.

The range of validity of the model extends from very dense liquids through the liquid-vapor transition region to very dilute gases. In the transition region the model gives a valid representation of systems undergoing a change of phase without recourse to the Maxwell construction. This feature is contingent on the fact that not all cells need be occupied, so that the model can portray systems with variable densities.

The Ising formalism provides a mathematical framework that is ideally suited to an investigation of this model. By virtue of the hard-core repulsive potential that has been assumed an exclusion principle is introduced into the system (no more than one particle per cell) which results in fermion-like behavior and establishes an isomorphism between Ising spin states and cell occupancy indices. This behavior manifests itself on various occasions throughout the study.

The assumptions inherent in the model do not materially detract from its usefulness and validity. The most artificial of these,
e.g., the periodic boundary conditions and the uncertainty imposed by the cell structure in knowing a particle's exact location, became negligible in the thermodynamic limit.

Multiple cell occupancy is not of interest in connection with the simple fluids to which this study is devoted and would reduce the fineness of the space grid, thereby impairing the validity of the model.

While the matrix formulation of the problem can be accomplished in a straightforward way, the spinor or algebraic technique of solution that proved so successful in the two-dimensional case does not lead to a solution of the present problem. The difficulty lies in the large number of bonds that connect the particles of the system with one another, the number approaching infinity in the thermodynamic limit. It is not possible because of this to write the operators representing these bonds as the spin representatives of commuting plane rotations, as one can do in the Onsager-Kaufman solution. The appropriate operator in the present instance is found to be part of the spin representative of a tensor transformation. No simple relationship exists between the eigenvalues of this transformation and those of the operator appropriate to the present model. However, by virtue of the cyclic nature which the periodic boundary conditions impart to the operator it is possible to diagonalize it by a Fourier-type transformation subject to meeting certain consistency conditions. In this way the partition function can be recast in the form of a very versatile and useful series expressed in terms of successive deviations from a perfectly ordered state.

The series solution of the partition function developed in this
study is absolutely and uniformly convergent for all values of the
Gibbs potential providing the interaction is an attractive one with
a hard-sphere repulsive core. This conclusion may well hold for
other potentials, but this was not investigated since the one above
is of primary interest in the case of simple fluids.

The series solution offers a convenient method for investigating
the analyticity of the partition function. The investigation confirms
the conclusions of Yang and Lee: The partition-function can have
no zeros on the real axis in the complex $y$-plane except in the
thermodynamic limit. For the potential considered, the zeros lie
all on the unit circle and occur in complex-conjugate pairs. Zeros
of the partition function on the real positive axis in the complex
$y$-plane may be thought of as particle sinks at which particles of
the system change from one phase to the other. The concept can be
extended to zeros lying off the real axis by considering these as
virtual sinks which assume physical reality only as the probability
associated with these points becomes real.

The one-dimensional model in which every particle interacts with
every other one, which is the basic model of this study, is topo-
logically equivalent to fluid models of higher dimensionality but
with more restricted interaction potentials. The cell model considered
in this study therefore offers a unified and very practical method
for treating two- and three-dimensional systems with a more limited
number of bonds as modifications of this more general one-dimensional
array. Starting from the series formulation of the one-dimensional
partition function, the method permits computation of the correct

$y = \exp(2\nu)$ is a modified activity; see equations (32), (34), and
(36) for definitions.
low-temperature series expansions for one, two, and three dimensional systems, using identical algebraic techniques. In the one-dimensional case the series can be summed, and by its agreement with the known, closed-form solution confirms the validity of the model and of the expansion. The two- and three-dimensional series obtained in this way for systems with nearest-neighbor interactions are identical with the corresponding series computed by other techniques. The method readily permits carrying the series approximations to higher order terms and is suited to computation of expansion coefficients by high-speed electronic computer. While this approach requires that the number of bonds remain finite, it is not necessary to restrict interactions to nearest neighbor ones. Additional bonds can be considered by the same technique, as long as their number per particle is sufficiently small.

The versatility of the model investigated permits it to be applied to fluid systems of many types. If in the limit of vanishing attractive interactions one allows the cell size to go to zero, the model reproduces an ideal gas in the thermodynamic limit. The equation of state of a fluid of hard rods, discs, or spheres is obtained in the same limit if the cell size is kept finite. The one-dimensional fluid with a hard repulsive core and only nearest-neighbor interactions exhibits many of the characteristics of real fluids, but undergoes no phase transition except for the degenerate one at absolute zero. Since it is possible to write its equation of state in closed, mathematically tractable form, the one-dimensional model with nearest-neighbor bonds offers a convenient medium for testing theories and concepts that do not depend on a change of phase.
Application of the model to another limiting case, that of a fluid in which all interactions are active but of infinitely long range, leads to a true phase transition for a one-dimensional system. This limit, in which the range parameter, γ, is allowed to go to zero, lies at the other end of the spectrum from the one-dimensional nearest-neighbor model. It can be viewed either as a one-dimensional system with extremely long-range forces or as an N-dimensional array in which all cells are nearest neighbors. In the thermodynamic limit, the system exhibits a phase transition at all finite temperatures.

Numerical analysis of finite systems shows very clearly the approach toward a true phase transition with increasing system size. Thus, the only indication of an incipient transition in a system of 20 cells is a certain characteristic inflection of the isotherm on a pressure-density diagram, while a system of 240 cells shows practically all of the characteristics of a fully-developed transition.

The series formulation of the partition function developed in this study lends itself very well to numerical analysis of finite one-, two-, and three-dimensional systems. Restrictions on computer time limited this investigation to systems of 15 cells or less. It is desirable, however, and seems feasible that algorithms could be developed which would permit analysis of larger systems. The small one-dimensional arrays investigated show surprisingly realistic thermodynamic behavior. Thus, the specific heat curves have well-defined maxima which become steeper and higher with increasing system size. These seem to approach a limiting critical temperature given approximately by \( t/6.45k \). The pressure-density and compressibility-density curves of these systems likewise show characteristics of an incipient phase
transition. The grand potential of such fluids at the critical temperature \((\beta_c)\) lies within a few per cent of the average experimental value for three-dimensional assemblies.

Interesting results are also obtained from an analysis of pair correlation functions for these fluids. It is found that correlation is almost perfect at temperatures well below the critical one. As the critical temperature is passed, long-range order changes markedly and quite rapidly to short-range order. This method of computing pair correlation functions offers a useful alternative to the usual integral equation technique. The text establishes the relationship between these two methods. However, the pair correlation functions computed from the present model are averaged over a cell and thus do not show the local fluctuations that usually characterize correlation curves.

Numerical analysis of small two- and three-dimensional systems reflects behavior very much akin to that found in one-dimensional models. While the same indications of incipient phase transitions are apparent, no actual change in phase is discernible in these small systems. This is in keeping with the gradual approach toward a phase transition with increasing system size observed in the \(\gamma \rightarrow 0\) approximation. Specific heat data peg the critical temperature of these systems at approximately \(\xi/1.7k\) and \(\xi/1.05k\) respectively. The three-dimensional value is almost exactly the same as the best estimates obtained by other methods. The two-dimensional value varies between wider limits because of boundary effects. However, it too, lies within a few per cent of the value given by the Onsager solution.
BIBLIOGRAPHY


APPENDICES
APPENDIX I

PARTITION FUNCTIONS FOR SMALL SYSTEMS

All partition functions below are for \( \nu = 0 \).

\[
Q_4 = 2 \left[ e^{4(\theta_1 + \theta_2)} + e^{4(\theta_1 - \theta_2)} + 4 \right]
\]

\[
Q_5 = 2 \left[ e^{10(\theta_1 + \theta_2)} + 5e^{2(\theta_1 + \theta_2)} + 5e^{2(\theta_1 - 3\theta_2)}
+ 5e^{2(-3\theta_1 + \theta_2)} \right]
\]

\[
Q_6 = 2 \left[ e^{6(2\theta_1 + 2\theta_2 + \theta_3)} + 6e^{2(2\theta_1 + 2\theta_2 + \theta_3)}
+ 6e^{2(2\theta_1 - 2\theta_2 - 2\theta_3)} + 6e^{2(2\theta_1 - 2\theta_2 - 2\theta_3)}
+ 3e^{2(-2\theta_1 + 2\theta_2 + 3\theta_3)} + 3e^{2(-2\theta_1 + 2\theta_2 + 3\theta_3)}
+ 3e^{2(-2\theta_1 + 2\theta_2 + 2\theta_3)} + 3e^{2(-2\theta_1 + 2\theta_2 + 2\theta_3)}
+ e^{2(-2\theta_1 + 2\theta_2 + 2\theta_3)} + e^{2(-2\theta_1 + 2\theta_2 + 2\theta_3)} \right]
\]

\[
Q_7 = 2 \left[ e^{14(\theta_1 + \theta_2 + \theta_3)} + 7e^{6(\theta_1 + \theta_2 + \theta_3)} + 7e^{2(3\theta_1 - \theta_2 - 3\theta_3)}
+ 7e^{2(3\theta_1 - \theta_2 - 3\theta_3)} + 7e^{2(-\theta_1 + 3\theta_2 - \theta_3)} + 7e^{2(-\theta_1 + 3\theta_2 - \theta_3)}
+ 7e^{2(-\theta_1 + 3\theta_2 - \theta_3)} + 7e^{2(-\theta_1 + 3\theta_2 - \theta_3)}
+ 14e^{2(0_1 + \theta_2 + \theta_3)} + 14e^{2(0_1 + \theta_2 + \theta_3)}
+ 2(0_1 + \theta_2 + \theta_3) + 2(0_1 + \theta_2 + \theta_3)
+ 2(0_1 + \theta_2 + \theta_3) \right]
\]

\[
Q_9 = 2 \left[ e^{18(\theta_1 + \theta_2 + \theta_3 + \theta_4)} + 9e^{10(\theta_1 + \theta_2 + \theta_3 + \theta_4)} \right]
\]
\[ 2(-361+62-383+64) + 2(-381-382+583-364) + 2(-361-362+63+64) + 2(-381-362+983-364) + 2(-301-302+303-304) + 2(-301-302+303+304) + 2(-301-302-303+304) + 2(-301-302-303-304) + 2(-301+302-303+304) + 2(-301+302-303-304) + 2(-301+302+303+304) + 2(-301+302+303-304) \]
A matrix formulation of the problem with which this paper is concerned was given in Chapter III and a matrix solution was discussed there. An alternative, spinor algebraic approach to the problem will be discussed in this appendix. The techniques used are akin to those employed by Onsager and Kaufman in solving the two-dimensional Ising problem. Starting from equation (94) in Chapter III, the method attempts to determine the eigenvalues of the operator \( S \) by attempting to establish a homomorphism between \( S \) and the group of orthogonal rotations. If this were possible one could readily determine the eigenvalues of the rotation operators involved and deduce from these the corresponding eigenvalue spectrum of \( S \).

In order to reduce the problem to its simplest terms, we shall consider only the case \( v = 0 \), i.e., \( S_2 = 1 \). The task is then to determine the eigenvalues of

\[
S_1 = \exp \left\{ \sum_{r=1}^{N} \sum_{s=1}^{N} Z_r Z_{r+s} \right\} = \prod_{r=1}^{N} \prod_{s=1}^{N} e^{Z_r Z_{r+s}} \quad (II-1)
\]

\[
= \prod_{r=1}^{N} \prod_{s=1}^{N} D_{rs}
\]
In the representation adopted in Chapter III, the operator \( D_{rs} \) is of course a \( 2^N \times 2^N \) matrix.

To proceed it is necessary to define a set of matrices that are the generators of a complete set of linearly independent operators that span the space of the operator \( S \). Since we have seen that the \( Z_k \)'s form part of a \( 2^N \)-dimensional quaternion algebra, the base matrices must also be members of such an algebra, and we require that they satisfy the appropriate anticommutation relations:

\[
\Gamma_{\alpha} \Gamma_{\beta} + \Gamma_{\beta} \Gamma_{\alpha} = [\Gamma_{\alpha}, \Gamma_{\beta}]_+ = 2\delta_{\alpha\beta}
\]  

\((\alpha = 1, 2, \ldots, 2N)\)

\((\beta = 1, 2, \ldots, 2N)\)

The base matrices of the space are then the \( \Gamma \)'s and all possible products of \( \Gamma \)'s. Since our representation is of order \( 2^N \), the operators in this space have \( 2^N \times 2^N = 2^{2N} \) independent elements. Hence \( 2^{2N} \) independent matrices are required for a complete base. Suppose now that there are \( m \) \( \Gamma \) matrices satisfying equation (II-2). Then there are \( \binom{m}{1} = m \) basic matrices, \( \binom{m}{2} \) products of two \( \Gamma \)'s, \( \binom{m}{3} \) products of three of them, etc. Or, altogether, \( \sum_{r=1}^{m} \binom{m}{r} = \sum_{r=0}^{m} \binom{m}{r} - 1 = 2^m - 1 \) such matrices. Adding to this the identity we have \( 2^m \) matrices in all. If these are to form a complete base, then \( 2^m = 2^{2N} \) or \( m = 2N \), i.e. there must be \( 2N \) \( \Gamma \)-matrices satisfying the relation (II-2). Thus, when \( N \) is 1 the space is the ordinary spinspace of dimension 2 and the two matrix generators are two of the three Pauli spin matrices. If
N = 2, then the four \( \Gamma \)'s are the four Dirac \( \gamma \)'s, etc. It is also necessary that we select a particular representation of the \( \Gamma \)'s. The most convenient one for representing the operator \( S \) is the following:

\[
\begin{align*}
\Gamma_1 &= X_1 \\
\Gamma_2 &= Y_1 \\
\Gamma_3 &= Z_1 X_2 \\
\Gamma_4 &= Z_1 Y_2 \\
&
\vdots
\end{align*}
\]

\[
\Gamma_{2\alpha-1} = Z_1 \cdots Z_{\alpha-1} X_\alpha \\
\Gamma_{2\alpha} = Z_1 \cdots Z_{\alpha-1} Y_\alpha
\]

It is readily verified that these satisfy the commutation relation (II-2). Suppose, for example, that \( \alpha < \beta \), then:

\[
[\Gamma_{2\alpha-1}, \Gamma_{2\beta-1}]_+ = (Z_1 \cdots Z_{\alpha-1} X_\alpha) (Z_1 \cdots Z_{\beta-1} X_\beta) + (Z_1 \cdots Z_{\beta-1} X_\beta) (Z_1 \cdots Z_{\alpha-1} X_\alpha)
\]

\[
= X_\alpha Z_{\alpha-1} Z_{\alpha+1} \cdots Z_{\beta-1} X_\beta + Z_{\alpha} Z_{\alpha+1} \cdots Z_{\beta-1} X_\beta Z_\alpha
\]

\[
= i \left( -Y_\alpha Z_{\alpha+1} \cdots Z_{\beta-1} X_\beta + Y_\alpha Z_{\alpha+1} \cdots Z_{\beta-1} X_\beta \right)
\]

\[
= 0
\]

Conversely, if \( \alpha = \beta \), then:

\[
[\Gamma_{2\alpha-1}, \Gamma_{2\alpha-1}]_+ = 2 (Z_1 \cdots Z_{\alpha-1} X_\alpha) (Z_1 \cdots Z_{\alpha-1} X_\alpha) = 2I
\]

so that in general

\[
[\Gamma_{2\alpha-1}, \Gamma_{2\beta-1}]_+ = 2 \delta_{\alpha, \beta}
\]
Other combinations are readily proved in the same way.

Consider now the product:

\[ \Gamma_{2\alpha - 1} \Gamma_{2\alpha} = (Z_1 \cdots Z_{\alpha - 1} X) (Z_1 \cdots Z_{\alpha - 1} Y) \quad (\text{II-4a}) \]

\[ = iZ_{\alpha} \]

Thus:

\[ Z_{\alpha} = -i \Gamma_{2\alpha - 1} \Gamma_{2\alpha} = i \Gamma_{2\alpha} \Gamma_{2\alpha - 1} \quad (\text{II-4b}) \]

Then

\[ D_{rs} = e^{r \Gamma_{r+s} \theta_s} = e^{-\theta_s \Gamma_{2r} \Gamma_{2r-1} \Gamma_{2(r+s)} \Gamma_{2(r+s)-1}} \quad (\text{II-5}) \]

Before proceeding with the examination of this operator, let us investigate the simpler one,

\[ S_{\alpha,\beta} = e^{\phi \Gamma_{\alpha} \Gamma_{\beta}} \quad (\text{II-6}) \]

which is of the form of the operator occurring in the Onsager-Kaufman solution of the two-dimensional Ising model of a ferromagnet with nearest-neighbor interactions.

Now, if \( \alpha = \beta \), then \( S_{\alpha \alpha} = e^{\phi I} = e^{\phi I} \). If \( \alpha \neq \beta \), then

\[ S_{\alpha \beta} = e^{\phi \Gamma_{\alpha} \Gamma_{\beta}} = I + \phi \Gamma_{\alpha} \Gamma_{\beta} + \frac{1}{2} \phi^2 \Gamma_{\alpha} \Gamma_{\beta} \Gamma_{\alpha} \Gamma_{\beta} + \ldots \quad (\text{II-7a}) \]

\[ = I + \phi \Gamma_{\alpha} \Gamma_{\beta} + \frac{1}{2} \phi^2 \{ \Gamma_{\alpha} [\Gamma_{\beta}, \Gamma_{\alpha}] + \Gamma_{\beta} - \Gamma_{\alpha} \Gamma_{\beta} \} + \ldots \]

\[ = I + \phi \Gamma_{\alpha} \Gamma_{\beta} - \frac{1}{2} \phi^2 I - \frac{1}{3!} \phi^3 \Gamma_{\alpha} \Gamma_{\beta} + \ldots \]
Similarly,
\[
S^{-1}_{\alpha \beta} = e^{-\phi \Gamma_{\alpha \beta}} = I \cos \phi - \Gamma_{\alpha \beta} \sin \phi
\]  
\text{(II-7b)}

And
\[
S^{-1}_{\alpha \beta} S_{\alpha \beta} = (I \cos \phi - \Gamma_{\alpha \beta} \sin \phi) (I \cos \phi + \Gamma_{\alpha \beta} \sin \phi)
\]
\[
= I \cos^2 \phi + (\Gamma_{\alpha \beta} - \Gamma_{\alpha \beta}) \sin \phi \cos \phi
\]
\[
- \Gamma_{\alpha \beta} \Gamma_{\alpha \beta} \sin^2 \phi
\]
\[
= I (\cos^2 \phi + \sin^2 \phi) = I
\]

Now note that
\[
\Gamma_{2\alpha-1}^\dagger = (Z_1 \ldots Z_{\alpha-1} X_\alpha)^* = X_\alpha^* Z_{\alpha-1}^* \ldots Z_1^*
\]  
\text{(II-8)}

\[
= X_\alpha Z_{\alpha-1} \ldots Z_1 = Z_1 \ldots Z_{\alpha-1} X_\alpha = \Gamma_{2\alpha-1}
\]

and similarly for \( \Gamma_{2\alpha} \). Hence the \( \Gamma \)'s are hermitian. It follows then that \( S_{\alpha \beta} \) is a unitary operator, for:
\[
S_{\alpha \beta}^\dagger = e^{\phi (\Gamma_{\alpha \beta})^\dagger} = e^{\phi \Gamma_{\beta \alpha}} = e^{\phi \Gamma_{\beta \alpha}^\dagger} = e^{-\phi \Gamma_{\alpha \beta}}
\]  
\text{(II-9)}

Let us next examine the transformation \( S_{\alpha \beta}^{-1} \Gamma_\mu S_{\alpha \beta} \), and suppose first that \( \mu \neq \alpha \) and \( \mu \neq \beta \). Then:
\[
S_{\alpha \beta}^{-1} \Gamma_\mu S_{\alpha \beta} = (I \cos \phi - \Gamma_{\alpha \beta} \sin \phi) \Gamma_\mu (I \cos \phi
\]
\[
+ \Gamma_{\alpha \beta} \sin \phi)
\]
\[
= \Gamma_\mu (S_{\alpha \beta}^{-1} S_{\alpha \beta}) = \Gamma_\mu
\]
since then \( \Gamma_{\alpha \beta} \Gamma_{\mu} = \Gamma_{\mu} \Gamma_{\alpha \beta} \), so that this is an identity transformation. If, now, \( \mu = \alpha \), then

\[
S_{\alpha \beta}^{-1} \Gamma_{\alpha} S_{\alpha \beta} = \Gamma_{\alpha} (S_{\alpha \beta})^2 = \Gamma_{\alpha} (I \cos^2 \phi - I \sin^2 \phi) + 2 \Gamma_{\alpha} \Gamma_{\beta} \sin \phi \cos \phi
\]

\[
= \Gamma_{\alpha} (I \cos 2\phi + \Gamma_{\alpha} \Gamma_{\beta} \sin 2\phi)
\]

\[
= \Gamma_{\alpha} \cos 2\phi + \Gamma_{\alpha} \cos 2\phi
\]

while if \( \mu = \beta \), then

\[
S_{\alpha \beta}^{-1} \Gamma_{\beta} S_{\alpha \beta} = \Gamma_{\beta} (S_{\alpha \beta})^2 = \Gamma_{\beta} (I \cos 2\phi + \Gamma_{\alpha} \Gamma_{\beta} \sin 2\phi) (II-10c)
\]

\[
= \Gamma_{\beta} \cos 2\phi - \Gamma_{\alpha} \sin 2\phi
\]

If we designate \( 2\phi = \Theta \), then this can be summarized as follows:

\[
\Gamma_{\mu} = S_{\alpha \beta}^{-1}(\Theta) \Gamma_{\mu} S_{\alpha \beta}(\Theta) = \Gamma_{\mu} \quad (\mu \neq \alpha; \mu \neq \beta) (II-11a)
\]

\[
\Gamma_{\alpha} = S_{\alpha \beta}^{-1}(\Theta) \Gamma_{\alpha} S_{\alpha \beta}(\Theta) = \Gamma_{\alpha} \cos \Theta + \Gamma_{\beta} \sin \Theta \quad (II-11b)
\]

\[
\Gamma_{\beta} = S_{\alpha \beta}^{-1}(\Theta) \Gamma_{\beta} S_{\alpha \beta}(\Theta) = -\Gamma_{\alpha} \sin \Theta + \Gamma_{\beta} \cos \Theta \quad (II-11c)
\]

where \( \Gamma_{\mu} \) etc., denote the transformed matrices and \( S_{\alpha \beta}(\Theta) \)

\[
= e^{i\Theta} \Gamma_{\alpha} \Gamma_{\beta} \cdot \Gamma_{\mu} \cdot \Gamma_{\beta}
\]

Consequently, if we think of the \( 2N \) \( \Gamma \)'s as elements of a vector in a \( 2N \)-dimensional space and if we define an operator in that space as follows:
\[
\begin{bmatrix}
1 & 0 & 0 & \ldots & 0 \\
0 & 1 & 0 & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & \ldots & 0 \\
0 & 0 & 0 & \ldots & 0 \\
\end{bmatrix}
\]

(II-12a)

\[
\omega(\theta) = \begin{bmatrix}
0 & 0 & 0 & \ldots & \cos \theta & \sin \theta & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \ldots & -\sin \theta & \cos \theta & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \ldots & 0 & 0 & 1 \\
\end{bmatrix}
\]

\[
\begin{array}{ccc}
\alpha & \beta \\
\text{row} & \text{column} & \text{column}
\end{array}
\]

and

\[
\mathbf{r} = \left| \mathbf{r}_{1}, \mathbf{r}_{2}, \ldots, \mathbf{r}_{2N} \right>
\]

(II-12b)

then we can write this same transformation:

\[
\bar{\mathbf{r}} = \omega \mathbf{r}
\]

(II-13a)

or

\[
\bar{\mathbf{r}}_{\mu} = \sum_{\nu=1}^{2N} \omega_{\mu \nu}(\theta) \mathbf{r}_{\nu}
\]

(II-13b)

We note that \( \omega^{\dagger} = \omega \), and

\[
\omega^{\dagger} \omega = \bar{\omega} \omega = \mathbf{I}
\]

so that \( \omega^{\dagger} = \bar{\omega} = \omega^{-1} \)

meaning that the operator \( \omega \) is orthogonal. One readily verifies that the commutation relations are preserved under this transformation:
\[
\begin{bmatrix}
\tilde{\Gamma}_{\mu} \omega \nu \beta \\
\end{bmatrix} + \sum_{\alpha=1}^{2N} \sum_{\beta=1}^{2N} \begin{bmatrix}
\omega_{\mu} \alpha \omega_{\nu} \beta \gamma_{\alpha} \\
\end{bmatrix} + \sum_{\alpha=1}^{2N} \sum_{\beta=1}^{2N} \omega_{\mu} \omega_{\nu} \delta_{\alpha, \beta} \\
= 2 \begin{bmatrix}
\omega_{\mu} \omega_{\nu} \alpha \\
\end{bmatrix} + 2 \alpha \\
= 2 \delta_{\mu \nu}
\] (II-14)

Consequently the transformation \( \omega \) is an automorphism analogous to a rotation in the 2N-dimensional space. The \( S \) matrices are the spin representatives of these rotations. It must be observed, however, that the mapping from the \( \omega \)'s to the \( S \)'s is not one-to-one. To see this let \( \alpha \) be any complex number; then, if we let \( \tilde{S}_{\mu \nu} = e^{2 \pi \alpha} \begin{bmatrix}
\tilde{\Gamma}_{\mu} \omega \nu \beta \\
\end{bmatrix} \),

\[
\tilde{\Gamma} = S^{-1} \Gamma S = \tilde{S}^{-1} \Gamma \tilde{S}.
\]

\( \omega \) therefore defines its spin representative \( S \) only within an arbitrary phase factor. The arbitrariness can be partially removed by imposing additional conditions on \( S \) (see for example reference 20); however, even then the mapping remains 2 to 1, i.e. \( e^\alpha \) may still assume the values \( \pm 1 \).

The eigenvalues of \( \omega \) are of course readily determined
to be $e^{i\theta}$ and $e^{-i\theta}$ (nondegenerate) and $1$ ($\pi \cdot 2$)-fold degenerate). The rotations $\omega$, furthermore, commute as is readily shown, i.e. $\omega(\theta_1) \omega(\theta_2) = \omega(\theta_1 + \theta_2) = \omega(\theta_2) \omega(\theta_1)$ for the plane rotations considered here. Hence the $\omega$ matrices corresponding to the operator $S$ in equation (II-C) can be diagonalized simultaneously, giving eigenvalues $e^{+2i\phi_1}$, $e^{-2i\phi_1}$, etc. Consider now the spin representative of a rotation $\omega_{\alpha\beta}(\theta) \mapsto S_{\alpha\beta}(\theta) = e^{\frac{\theta}{2}\Gamma_{\alpha\beta}}$, and for convenience let $\alpha = 2r$, $\beta = 2r-1$, then

$$e^{\frac{\theta}{2}2r\Gamma_{2r-1}} = e^{\frac{i\theta}{2}r} = I \cos\left(\frac{\theta}{2}\right) + i 2r\Gamma_{2r-1} \sin\left(\frac{\theta}{2}\right)$$

$$= I \cos\left(\frac{\theta}{2}\right) + i 2r \sin\left(\frac{\theta}{2}\right)$$

$$= I(x)\ldots(x) \begin{bmatrix} \cos\frac{\theta}{2} & 0 \\ 0 & \cos\frac{\theta}{2} \end{bmatrix} (x)I(x)\ldots(x)I$$

$$+ I(x)\ldots(x) \begin{bmatrix} i \sin\frac{\theta}{2} & 0 \\ 0 & -i \sin\frac{\theta}{2} \end{bmatrix} (x)\ldots(x)I$$

$$= I(x)\ldots(x) \begin{bmatrix} e^{\frac{i\theta}{2}} & 0 \\ 0 & e^{-\frac{i\theta}{2}} \end{bmatrix} (x)\ldots(x)I$$

$r$-th factor
Hence we see that the eigenvalues of $S_{ab}$ are $e^{i\frac{\pi}{2}}$ and $e^{-i\frac{\pi}{2}}$, each occurring $2^{N-1}$ times. This does not change if $a$ and $b$ are arbitrary; only the distribution of eigenvalues along the diagonal of $S_{\rho}$ is affected thereby. Thus the eigenvalues of the spin representative of a product of commuting plane rotations with eigenvalues $e^{i2\phi_1}$, $e^{i2\phi_2}$, etc. are $e^{i(\phi_1 \pm \phi_2 \pm \ldots)}$ with all possible combinations of sign.

The eigenvalue problem is then essentially solved and the partition function can be obtained.$^{1,30}$

One would therefore like to follow the same route of analysis with the operator $D_{\rho_\pi}$ in equation (II-5). If that were possible the present problem would be solved. Unfortunately, it turns out that this operator is not the spin representative of a plane rotation, but rather is part of a tensor transformation, as will be shown now. Consider the operator

$$D_{\mu \nu \rho \sigma} = e^{\frac{\theta}{2} \Gamma_{\mu} \Gamma_{\nu} \Gamma_{\rho} \Gamma_{\sigma}} \quad \text{(II-15)}$$

Now, $(\Gamma_{\mu} \Gamma_{\nu} \Gamma_{\rho} \Gamma_{\sigma})^2 = I$ if $\mu \neq \nu \neq \rho \neq \sigma$, which we shall assume.

This is readily proved by using the commutation rule, equation (II-2). Then:

$$D_{\mu \nu \rho \sigma} = I + (\frac{\theta}{2}) \Gamma_{\mu} \Gamma_{\nu} \Gamma_{\rho} \Gamma_{\sigma} + \frac{(\frac{\theta}{2})^2}{2!} I \quad \text{(II-16)}$$
\[
\frac{(\theta/2)^3}{3!} + \frac{(\theta/2)^2}{2!} \Gamma_{\mu \nu \rho \sigma} + \ldots
\]

\[= I \cosh \left(\frac{\theta}{2}\right) + \sum_{\mu \nu \rho \sigma} \Gamma_{\mu \nu \rho \sigma} \sinh \left(\frac{\theta}{2}\right)\]

Let us examine first the properties of a related operator:

\[
G_{\mu \nu \rho \sigma} = e^{\frac{\theta}{2} (\Gamma_{\mu \nu} + \Gamma_{\rho \sigma})}
\]

(II-17)

and assume again that \(\mu, \nu, \rho, \) and \(\sigma\) are distinct. Noting that:

\[
(\Gamma_{\mu \nu} + \Gamma_{\rho \sigma})^2 = (\Gamma_{\mu \nu})^2 + \Gamma_{\mu \nu} \Gamma_{\rho \sigma} + \Gamma_{\rho \sigma} \Gamma_{\mu \nu}
\]

\[+ (\Gamma_{\rho \sigma})^2
\]

\[= 2 (\Gamma_{\mu \nu} \Gamma_{\rho \sigma} - I)
\]

we have:

\[
G_{\mu \nu \rho \sigma} = I + \frac{(\theta/2)}{2!} (\Gamma_{\mu \nu} + \Gamma_{\rho \sigma}) + \frac{(\theta/2)^2}{2!} 2(\Gamma_{\mu \nu} \Gamma_{\rho \sigma} - I)
\]

\[- \frac{(\theta/2)^3}{3!} 4(\Gamma_{\mu \nu} + \Gamma_{\rho \sigma}) - \frac{(\theta/2)^4}{4!} 8(\Gamma_{\mu \nu} \Gamma_{\rho \sigma} - I) + \ldots
\]

Thus:

\[
G_{\mu \nu \rho \sigma} = I \cos^2 \left(\frac{\theta}{2}\right) + (\Gamma_{\mu \nu} + \Gamma_{\rho \sigma}) \sin \left(\frac{\theta}{2}\right) \cos \left(\frac{\theta}{2}\right)
\]

(II-18)

\[+ \Gamma_{\mu \nu \rho \sigma} \sin^2 \left(\frac{\theta}{2}\right)
\]

where use was made of the trigonometric identities:

\[
\cos^2 \left(\frac{\theta}{2}\right) = \frac{1}{2} (1 + \cos \theta) = \frac{1}{2} \left(2 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} + \ldots\right)
\]
\[ \sin^2 \left( \frac{\theta}{2} \right) = \frac{1}{2} (1 - \cos \theta) = \frac{1}{2} \frac{\theta^2}{2!} - \frac{1}{2} \frac{\theta^4}{4!} + \ldots \]

It is possible to rewrite (II-18) in a more convenient way:

\[ G_{\mu \nu \rho \sigma} = \frac{1}{2} \left\{ I (1 + \cos \theta) + \left( \Gamma_{\mu \nu} + \Gamma_{\rho \sigma} \right) \sin \theta \right\} \]

\[ + \Gamma_{\mu \nu} \Gamma_{\rho \sigma} (1 - \cos \theta) \}

\[ = \frac{1}{2} \left\{ (I \cos \theta + \Gamma_{\mu \nu} \sin \theta) + (I \cos \theta + \Gamma_{\rho \sigma} \sin \theta) \right\} \]

\[ + I (1 - \cos \theta) + \Gamma_{\mu \nu} \Gamma_{\rho \sigma} (1 - \cos \theta) \}

\[ = \frac{1}{2} \left\{ S_{\mu \nu} (\theta) + S_{\rho \sigma} (\theta) + a(I \cosh \phi \]

\[ + \Gamma_{\mu \nu} \Gamma_{\rho \sigma} \sinh \phi) + bI \right\} \]

\[ = \frac{1}{2} \left\{ S_{\mu \nu} (\theta) + S_{\rho \sigma} (\theta) + aD_{\mu \nu \rho \sigma} (2\phi) + bI \right\} \]

where \( a \) and \( b \) are defined by:

\[ a \sinh \phi = (1 - \cos \theta) = a \cosh \phi + b \] (II-20a)

If we let \( a = \text{sech} \phi \), then \( b = \tanh \phi - 1 \) and the relationship defining \( \theta \) in terms of \( \phi \) is:

\[ \tanh \phi = 1 - \cos \theta \] (II-20b)

We must next investigate the properties of the operator \( G \). The analysis is simplified if we note that

\[ [\Gamma_{\mu \nu}, \Gamma_{\rho \sigma}] = 0 \quad (\mu, \nu, \rho, \sigma \text{ distinct}) \] (II-21)

so that

\[ G_{\mu \nu \rho \sigma} (\theta) = e^{\frac{\theta}{2} (\Gamma_{\mu \nu} + \Gamma_{\rho \sigma})} = e^{\frac{\theta}{2} \Gamma_{\mu \nu}} e^{\frac{\theta}{2} \Gamma_{\rho \sigma}} \] (II-22)
Consequently:

\[ G_{\mu \nu \rho \sigma}^{-1} G_{\mu \nu \rho \sigma} = S_{\mu \nu}^{-1} S_{\rho \sigma}^{-1} S_{\mu \nu} S_{\rho \sigma} \]  

\[ = S_{\mu \nu}^{-1} S_{\mu \nu} S_{\rho \sigma}^{-1} S_{\rho \sigma} \]

\[ = I \]

so that \( G \) is also a unitary operator. (Of course \( G^+ = G^{-1} \) as is readily shown using equation (II-9).) Consider now the following transformations:

\[ \Gamma_{\mu \nu} \Gamma_{\mu \nu} = G_{\mu \nu \rho \sigma}^{-1} \Gamma_{\mu \nu} G_{\mu \nu \rho \sigma} = S_{\mu \nu}^{-1} S_{\rho \sigma}^{-1} \Gamma_{\mu \nu} S_{\rho \sigma} \]  

\[ = S_{\mu \nu}^{-1} \Gamma_{\mu \nu} S_{\rho \sigma} \]

\[ = \Gamma_{\mu \nu} S_{\rho \sigma}^{-1} S_{\mu \nu} \]

\[ = \Gamma_{\mu \nu} \]

\[ \Gamma_{\rho \sigma} \Gamma_{\mu \nu} = G_{\mu \nu \rho \sigma}^{-1} \Gamma_{\rho \sigma} G_{\mu \nu \rho \sigma} = \Gamma_{\rho \sigma} \]  

\[ \Gamma_{\alpha \beta} \Gamma_{\alpha \beta} = G_{\mu \nu \rho \sigma}^{-1} \Gamma_{\alpha \beta} G_{\mu \nu \rho \sigma} = \Gamma_{\alpha \beta} \]  

\[ (\alpha, \beta \neq \mu, \nu, \rho, \sigma) \]  

\[ \Gamma_{\mu \rho} \Gamma_{\rho \sigma} = G_{\mu \nu \rho \sigma}^{-1} \Gamma_{\mu \rho} G_{\mu \nu \rho \sigma} = S_{\mu \nu}^{-1} \Gamma_{\mu \rho} S_{\nu \rho \sigma}^{-1} \Gamma_{\rho \sigma} \]

\[ = (\Gamma_{\mu} \cos \theta + \Gamma_{\nu} \sin \theta) (\Gamma_{\rho} \cos \theta + \Gamma_{\sigma} \sin \theta) \]

\[ = \Gamma_{\mu} \cos^2 \theta + (\Gamma_{\nu} \Gamma_{\rho} + \Gamma_{\mu} \Gamma_{\sigma}) \sin \theta \cos \theta + \Gamma_{\nu} \Gamma_{\rho} \sin^2 \theta \]

\[ \Gamma_{\mu \sigma} \Gamma_{\mu \rho} = G_{\mu \nu \rho \sigma}^{-1} \Gamma_{\mu \sigma} G_{\mu \nu \rho \sigma} = S_{\mu \nu}^{-1} \Gamma_{\mu \sigma} S_{\nu \rho \sigma}^{-1} \Gamma_{\rho \sigma} \]

\[ = \Gamma_{\mu \sigma} \cos^2 \theta + (\Gamma_{\nu} \Gamma_{\sigma} - \Gamma_{\mu} \Gamma_{\rho}) \sin \theta \cos \theta - \Gamma_{\nu} \Gamma_{\rho} \sin^2 \theta \]
Other transformations follow the same pattern. If, therefore, we define a new vector $X$ whose components are the dyadics $\Gamma^\alpha_\beta$, then these transformations can be represented as follows:

$$
\overline{X} = \begin{bmatrix}
\Gamma^\mu_\rho & \\
\Gamma^\mu_\sigma & \\
\Gamma^\nu_\rho & \\
\Gamma^\nu_\sigma & \\
\end{bmatrix}
$$

$$(\text{II}-24f)$$

$$
X = \begin{bmatrix}
\cos^2\theta & \sin\theta & \sin\theta & \sin^2\theta \\
\cdot\cos\theta & \cdot\cos\theta & \cdot\cos\theta & \\
-\sin\theta & \cos^2\theta & -\sin^2\theta & \sin\theta \\
\cdot\cos\theta & \cdot\sin^2\theta & \cdot\cos\theta & \\
-\sin\theta & -\sin^2\theta & \cos^2\theta & \sin\theta \\
\cdot\cos\theta & \cdot\sin\theta & \cdot\cos\theta & \\
\sin^2\theta & -\sin\theta & -\sin\theta & \cos^2\theta \\
\cdot\cos\theta & \cdot\cos\theta & \\
\end{bmatrix}
$$

Here only the non-invariant elements of $X$ and the non-identity elements of $\Omega$ have been displayed. The vector $X$ consists of all possible dyadics, including the identities; hence it has $(2N)^2 = 4N^2$ elements. We note that

$$
\Omega_{\mu\nu\rho\sigma}(\theta) = \omega_{\mu\nu}(\theta)(x)\omega_{\rho\sigma}(\theta)
$$

while $X = \Gamma(x)\Gamma$

where the vector $\Gamma$ is defined by equation (II-12b). Thus $\Omega$ is a tensor transformation transforming $\Gamma$ dyadics into themselves. Using covariant-contravariant notation and
the summation convention we can define the following tensor:

\[ T^{\mu \nu} = \Gamma^{\mu} \Gamma^{\nu} \]  

(II.25)

and then write the transformation as follows:

\[ \tilde{T}^{\mu \nu} = \Omega^{\mu \nu}_{\alpha \beta} \tilde{T}^{\alpha \beta} \]  

(II-26)

It follows, then, that the operator \( G \) is the spin representative of a tensor transformation, while the operator \( D \) is not a spin representative, but is associated with the operator \( G \). Although the eigenvalues of \( \Omega \) can be found readily, those belonging to the operator \( S_1 \), which consists of products of operators of the form of \( D \), cannot be determined in any straightforward way from those of \( \Omega \). Thus the problem does not permit of a solution analogous to that of the two-dimensional Ising model. In the two-dimensional case one is only concerned with nearest neighbor interactions. It is therefore possible in that case to find representations in which both the horizontal and vertical bond operators are the spin representatives of commuting rotations. In the present problem all interactions are active. Hence one has all the complications of the three-dimensional Ising model and many more. The simplifications of the two-dimensional Ising model can no longer be made. While it is possible to find the eigenvalues of \( G \) from those of \( \Omega \), it has not proved possible to determine those of \( S_1 \) therefrom.
APPENDIX III

COMPUTER ANALYSIS OF SERIES EXPANSION COEFFICIENTS

The computer programs in this appendix are designed to show the equivalence of equations (199) and (221)(c) in the text. The program in Section A, written in PL-1, computes the coefficients of \( a = (x - 1) \) directly from the following equation:

\[
\hat{\tau}_n = \frac{1}{n!} \sum_{q_1=1}^{n} \ldots \sum_{q_n=1}^{n} \prod_{r=1}^{n} \prod_{s=1}^{n} (1 + a \Delta(q_r-q_s),1) \quad (r < s)
\]

\[
= \sum_{q_1=q_2=\ldots=q_n}^{\infty} \prod_{r=1}^{n} \prod_{s=1}^{n} (1 + a \Delta(q_r-q_s),1) \quad (r < s)
\]

\[
= \sum_{r=0}^{\infty} C_r a^r
\]

The program in Section B, written in FORTRAN IV, computes the same coefficients from the following equation:

\[
\hat{\tau}_n = \frac{N}{n} \sum_{\ell=0}^{n-1} \sum_{K=1}^{n-\ell} \binom{n-1}{\ell} \binom{n-1}{n-K} (n-K,a,\ell) \quad (221c)
\]

\[
= \sum_{r=0}^{\infty} C_r a^r
\]

Comparison shows that the coefficients computed by these two methods are identical and that the two series are
therefore equivalent.

In order to keep machine time within reasonable limits computation was restricted to \( N \leq 20 \).
A. Program for Computation of Expansion Coefficients from Equation (199).

The fixed-point variable $M$ in this program corresponds to the index $n$ in the equation (199). The vector COEFF in the program designates the desired expansion coefficients.
SUBCAO: "PROCEDURE OPTIONS(X):

DECLARE (SUB(0:10), COEF1(0:50), COEF2(0:50), COEF3(0:50));

ON ERROR (SYSTEM) GO TO X;

COEFF = 0;
GET DATA (M, N);
A: DO (I = 1 TO N);
   DO (J = 1 TO N);
   IF (I^2) <= I(J) THEN GO TO C2;
   DO (J = 1 TO N);
   IF (I^2) <= I(J) THEN GO TO C3;
   DO (J = 1 TO N);
   IF (I^2) <= I(J) THEN GO TO C4;
   DO (J = 1 TO N);
   IF (I^2) <= I(J) THEN GO TO C5;
   DO (J = 1 TO N);
   IF (I^2) <= I(J) THEN GO TO C6;
   DO (J = 1 TO N);
   IF (I^2) <= I(J) THEN GO TO C7;
   DO (J = 1 TO N);
   IF (I^2) <= I(J) THEN GO TO C8;
   SUP = 0;
   DO (K = 1 TO N-1);
   DO (J = K+1 TO N);
   IF (I(K) = I(J)+1) THEN L = L+1;
   IF (I(K) = I(J)-1) THEN L = L+1;
   IF (I(K) = I(J)+N-1) THEN L = L+1;
   IF (I(K) = I(J)-N+1) THEN L = L+1;
   IF (L = L+1) THEN L = L+1;
   END;
   END;
   IF (SUB(1)) > (SUB(2)) THEN J1 = SUB(1);
   ELSE J1 = SUB(2);
   COEF1(J1) = 0;
   COEF2(J1) = 0;
   TEMP = 1;
   COEF1(0) = 1;
   DO (J = 1 TO SUB(1));
   TEMP = TEMP*(SUB(1) - J-1)/J;
   COEF1(J) = TEMP;
   END;
   COEF2(0) = 1;
   TEMP = 1;
   DO (J = 1 TO SUB(2));
   TEMP = TEMP*(SUB(2) - J-1)/J;
   COEF2(J) = TEMP;
   END;
   J1 = 1:
   DO (K = 1 TO J1):
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SUMCALC: PROCEDURE OPTIONS(HAIN);

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B. Program for Computation of Expansion Coefficients from Equation (221).

M in the program corresponds to n in equation (221c). The vector C designates the desired expansion coefficients.
```plaintext
COEFFICIENTS IN POLYNOMIAL EXPANSION OF NN PARTITION FUNCTION

DIMENSION JF(25), JC(25, 25), C(25)
READ (1, 40) M, N
WRITE (3, 25) M, N
JF(1) = 6

DO 5 K = 1, N
  5 JF(K+1) = JF(K) * K

DO 10 K = 1, L
  10 JC(K, L) = JF(K) / (JF(L) * JF(K-L))

DO 20 K = 1, M
  20 WRITE(3, 30) K, C(K)

STOP

WRITE(3, 30) K, C(K)
END

DATA

M = 5  N = 10
R = 1  C(R) = 252.00
R = 2  C(R) = 562.00
R = 3  C(R) = 420.00
R = 4  C(R) = 120.00
R = 5  C(R) = 10.00

M = 6  N = 12
R = 0  C(R) = 924.00
R = 1  C(R) = 2520.00
R = 2  C(R) = 2520.00
R = 3  C(R) = 1120.00
R = 4  C(R) = 210.00
R = 5  C(R) = 120.00
R = 6  C(R) = 12.00

M = 6  N = 13
R = 0  C(R) = 1272.00
R = 1  C(R) = 4770.00
R = 2  C(R) = 3900.00
R = 3  C(R) = 1560.00
R = 4  C(R) = 260.00
R = 5  C(R) = 14.00

M = 6  N = 14
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R = 1  C(R) = 6930.00
R = 2  C(R) = 5775.00
R = 3  C(R) = 2100.00
R = 4  C(R) = 315.00
R = 5  C(R) = 14.00

M = 6  N = 15
R = 0  C(R) = 1115.00
R = 1  C(R) = 2550.00
R = 2  C(R) = 2025.00
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R = 4  C(R) = 110.00
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APPENDIX IV

MATRIX DERIVATION OF THE ONE-DIMENSIONAL ISING MODEL FERROMAGNET PARTITION FUNCTION

Symbols used in the derivation below are identical to those used in the text.

\[ H = -J \sum_{r=1}^{N} \sigma_r \sigma_{r+1} - B\mu \sum_{r=1}^{N} \sigma_r \]

\[ Q_N = \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp \{\beta (J \sum_{r=1}^{N} \sigma_r \sigma_{r+1} + B\mu \sum_{r=1}^{N} \sigma_r)\} \]

\[ = \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} \exp \{\epsilon \sum_{r=1}^{N} \sigma_r \sigma_{r+1} + \nu \sum_{r=1}^{N} \sigma_r\} \]

\[ = \sum_{\sigma_1=-1}^{1} \cdots \sum_{\sigma_N=-1}^{1} <\sigma_1|P|\sigma_2><\sigma_2|P|\sigma_3>\cdots<\sigma_N|P|\sigma_1> \]

\[ = \text{Tr} \{P^N\} \]

where

\[ P = \begin{pmatrix} - & e^{\epsilon+\nu} & e^{-\epsilon} \\ e^{-\epsilon} & e^{\epsilon-\nu} & - \\ - & e^{-\epsilon} & e^{\epsilon-\nu} \end{pmatrix} \]

\(\epsilon = \beta J ; \quad \nu = \beta \mu B\)

\(\lambda_+ + \lambda_- = |P| = e^{2\epsilon} - e^{-2\epsilon} = \sinh 2\epsilon\)

\(\lambda_+ - \lambda_- = \text{Tr}(P) = 2e^\epsilon \cosh \nu\)
\[ \lambda^2 - 2e^\varepsilon \lambda \cosh \varphi + 2 \sinh 2\varepsilon = 0 \]

\[ \lambda_+ = e^\varepsilon \left[ \cosh \varphi + \sqrt{\cosh^2 \varphi - 2e^{-2\varepsilon} \sinh 2\varepsilon} \right] \]

\[ \lambda_- = e^\varepsilon \left[ \cosh \varphi - \sqrt{\cosh^2 \varphi - 2e^{-2\varepsilon} \sinh 2\varepsilon} \right] \]

\[ Q_N = \text{Tr}\{p^N\} = \lambda_+^N + \lambda_-^N \]

\[ = e^{N\varepsilon} \cosh^N \varphi \left\{ (1 + \sqrt{1+W})^N + (1 - \sqrt{1+W})^N \right\} \]

\[ W = (x_1^{-1} - 1) \sech^2 \varphi \quad ; \quad x_1 = e^{4\varepsilon} \]

\[ Q_N(\varphi=0) = e^{N\varepsilon} \left\{ (1 + e^{-2\varepsilon})^N + (1 - e^{-2\varepsilon})^N \right\} \]

\[ = 2^N \left[ \cosh^N \varepsilon + \sinh^N \varepsilon \right] \]
APPENDIX V

PROOF OF THE VALIDITY OF THE SOLUTION IN THE ONE-DIMENSIONAL NEAREST-NEIGHBOR APPROXIMATION

It is shown in the text that in the one-dimensional nearest-neighbor approximation the solution, equation (178), takes the following form:

\[ Q = 2A \left\{ \cosh (N\nu) + \sum_{n=1}^{[N/2]} \sum_{k=1}^{N-n-1} \binom{n}{k} (N-n-1)^{k-1} x_1^{-k} \right\} \]

\[ \times \cosh \left[ (N-2n)\nu \right] \left( 1-\frac{1}{2} \delta_{n,N/2} \right) \]

In Appendix IV the equivalent partition function for the one-dimensional Ising ferromagnet is derived by a simple matrix method with the following result:

\[ Q_N = e^{N\nu} \cosh^N \nu \left\{ (1 + \sqrt{1+W})^N + (1 - \sqrt{1+W})^N \right\} \quad (IV-1) \]

\[ W = (x_1^{-1} - 1) \operatorname{sech}^2 \nu \quad (IV-2) \]

It will be proved below that these two expressions are indeed equivalent. To proceed with the proof, it is desirable to transform equation (IV-1) to the following form:

\[ Q_N = e^{N\nu} \cosh^N \nu \left\{ (1 + \sqrt{1+W})^N + (1 - \sqrt{1+W})^N \right\} \quad (IV-1a) \]

\[ = 2e^{N\nu} \cosh^N \nu \sum_{n=0}^{[N/2]} \sum_{k=0}^{N} \binom{n}{k} (\frac{N}{2n}) W^k \]

\[ = 2e^{N\nu} \cosh^N \nu \sum_{n=0}^{[N/2]} \sum_{k=0}^{N} \binom{n}{k} (\frac{N}{2n}) \cosh^{-2k} \nu (x_1^{-1} - 1)^k \]
\[ N = 2e^{N_\epsilon} \cosh N_v \sum_{n=0}^{\lceil N/2 \rceil} \sum_{k=0}^{n} \sum_{m=0}^{k} \left( \begin{array}{c} N \atop 2n \end{array} \right) \left( \begin{array}{c} n \atop k \end{array} \right) \left( \begin{array}{c} k \atop m \end{array} \right) (-1)^{k-m} x_1^{-m} \cdot \cosh^{-2k}(v) \]

Since for the ferromagnet \( A = e^{N_\epsilon} \), the proposed proof resolves itself into showing the equivalence of the following two expressions:

\[ \cosh(Nv) + \sum_{n=1}^{\lceil N/2 \rceil} \sum_{k=1}^{n} \sum_{l=1}^{N-n-1} \left( \begin{array}{c} N \atop n \end{array} \right) \left( \begin{array}{c} n-1 \atop k-1 \end{array} \right) x_1^{-k} \cosh \left[ \left( N-2n \right)v \right] \cdot \left( 1 - \frac{1}{2} \delta_{n,N/2} \right) \quad (V-1) \]

\[ \cosh^N(v) \sum_{n=0}^{\lceil N/2 \rceil} \sum_{k=0}^{n} \sum_{m=0}^{k} \left( \begin{array}{c} N \atop 2n \end{array} \right) \left( \begin{array}{c} n \atop k \end{array} \right) \left( \begin{array}{c} k \atop m \end{array} \right) (-1)^{k-m} x_1^{-m} \cosh^{-2k}(v) \quad (V-2) \]

Consider first the case \( m = 0 \) in the second expression. If the equivalence is to hold in that instance we must show that

\[ \cosh^N(v) \sum_{n=0}^{\lceil N/2 \rceil} \sum_{k=0}^{n} \left( \begin{array}{c} N \atop 2n \end{array} \right) \left( \begin{array}{c} n \atop k \end{array} \right) (-1)^k \cosh^{-2k}(v) \quad (V-3) \]

\[ = \cosh(Nv) \]

We observe from the expansion (IV-1a) above (see also equation (225) in the text) that

\[ \cosh^{N}(v) \sum_{n=0}^{\lceil N/2 \rceil} \sum_{k=0}^{n} \left( \begin{array}{c} N \atop 2n \end{array} \right) \left( \begin{array}{c} n \atop k \end{array} \right) (-1)^k \cosh^{-2k}(v) \]

\[ = \frac{1}{2} \cosh^{N}(v) \left[ (1 + \sqrt{1-\text{sech}^2 v})^N + (1 - \sqrt{1-\text{sech}^2 v})^N \right] \]
\[ = \frac{1}{2} \cosh^N(v) \left[ (e^v \cosh^{-1} v)^N + (e^{-v} \cosh^{-1} v)^N \right] \]

\[ = \frac{1}{2} (e^{Nv} + e^{-Nv}) = \cosh (Nv) \]

as was to be shown. For \( m = 1 \) the identity that must be shown to hold is:

\[ N x _i = 1 \sum_{n=1}^{[N/2]} \cosh \left[ (N-2n)v \right] \left( 1 - \frac{1}{2} \delta_n, N/2 \right) \quad (v-4) \]

\[ = x \sum_{n=1}^{[N/2]} \cosh^N(v) \sum_{n=0}^{N} \sum_{K=0}^{N} \frac{n}{2n} (n) (n) (-1)^K \cosh^{-2K}(v) \]

To establish this let us make the following definition:

\[ f(N, v) = \cosh Nv \text{ sech}^N(v) = \sum_{n=0}^{[N/2]} \sum_{K=0}^{N} \frac{n}{2n} (n) (n) (-1)^K \cosh^{-2K}(v) \quad (v-5) \]

Then:

\[ \frac{\partial}{\partial v} f(N, v) = \sum_{n=0}^{[N/2]} \sum_{K=0}^{N} \frac{n}{2n} (n) (n) (-1)^K \cosh^{-2K}(v) \sinh (v) \]

\[ = 2 \tanh (v) \sum_{n=1}^{[N/2]} \sum_{K=1}^{N} \frac{n}{2n} (n) (n) (-1)^K \cosh^{-2K}(v) \]

\[ = N \cosh (Nv) \text{ sech}^N(v) - \cosh (Nv) \tanh (v) \text{ sech}^N(v) \]

\[ = N \cosh (Nv) \sinh (Nv) - \cosh (Nv) \tanh (v) \]

Therefore:

\[ \cosh^N(v) \sum_{n=1}^{[N/2]} \sum_{K=1}^{N} \frac{n}{2n} (n) (n) (-1)^K \cosh^{-2K}(v) (v-6) \]

\[ = \frac{N}{2} \left( \sinh (Nv) \coth (v) - \cosh (Nv) \right) \]
\begin{equation}
\frac{e^{(N-1)v} - e^{-(N-1)v}}{e^v - e^{-v}}
\end{equation}

\begin{equation}
= \sum_{K=0}^{\infty} (e^{(N-2K-2)v} - e^{-(N+2K)v})
\end{equation}

\begin{equation}
= N \sum_{K=1}^{[N/2]} \cosh [(N-2K)v] \left(1 - \frac{1}{2} \delta_{K,N/2}\right)
\end{equation}

Thus equation (V-4) is proved and the equality holds for 
\(m = 0\) and \(m = 1\). Suppose now that the equality to be estab-
lished between expressions (V-1) and (V-2) holds for \(m = m\), 
i.e. suppose that:

\begin{equation}
\sum_{n=m}^{[N/2]} \sum_{K=1}^{n} \binom{N}{n} \binom{n}{K} (-1)^{K-m} \cosh^{-2K(v)}
\end{equation}

\begin{equation}
= \frac{N}{m} \cosh^{-N(v)} \sum_{n=m}^{[N/2]} \binom{n-1}{m-1} \binom{N-n-1}{m} \cosh [(N-2n)v] \left(1 - \frac{1}{2} \delta_{n,N/2}\right)
\end{equation}

We wish to show then that it holds for \(m = m+1\), i.e. we 
wish to show that then:

\begin{equation}
\sum_{n=m+1}^{[N/2]} \sum_{K=m+1}^{n} \binom{n}{2n} \binom{n}{K} \binom{K}{m+1} (-1)^{K-m-1} \cosh^{-2K(v)}
\end{equation}

\begin{equation}
= \left(\frac{N}{m+1}\right) \cosh^{-N(v)} \sum_{n=m+1}^{[N/2]} \binom{n-1}{m} \binom{N-n-1}{m} \cosh [(N-2n)v] \left(1 - \frac{1}{2} \delta_{n,N/2}\right)
\end{equation}

Now,

\begin{equation}
\sum_{n=m+1}^{[N/2]} \binom{n-1}{m} \binom{N-n-1}{m} \cosh [(N-2n)v] \left(1 - \frac{1}{2} \delta_{n,N/2}\right)
\end{equation}
\[
\begin{align*}
\left[\frac{N}{2}\right] &= \frac{1}{2} \left\{ \frac{N}{2} \right\} (N-n-1)(n-m)(N-n-m) \cosh [(N-2n)\nu] \\
&\quad \cdot \left( 1 - \frac{1}{2} \delta_{n,N/2} \right)
\end{align*}
\]

Or:
\[
\begin{align*}
\frac{N}{m+1} \cosh^{-N}(\nu) &= \left[\frac{N}{2}\right] \sum_{n=m+1}^{\left\lfloor N/2 \right\rfloor} \frac{n-1}{m} \frac{(N-n-1)(n-m)(N-n-m)}{(n-1)(m-1)(n-m)} \\
&= \left( \frac{N}{m+1} \right) \text{sech}^N(\nu) \sum_{n=m}^{\left\lfloor N/2 \right\rfloor} \frac{n-1}{m} \frac{(N-n-1)(n-m)(N-n-m)}{(n-1)(m-1)(n-m)} \\
&\quad \cdot \cosh [(N-2n)\nu] \left( 1 - \frac{1}{2} \delta_{n,N/2} \right)
\end{align*}
\]

Also,
\[
\begin{align*}
\left[\frac{N}{2}\right] &= \sum_{n=m}^{N} \sum_{K=m}^{n} \frac{N}{2n} \frac{K}{K} \frac{(-1)^{K-m-1}}{m+1} \cosh^{-2K}(\nu) \\
&= \left( \frac{1}{m+1} \right) \left[\frac{N}{2}\right] \sum_{n=m}^{N} \sum_{K=m}^{n} \frac{N}{2n} \frac{K}{K} \frac{(-1)^{K-m-1}}{m+1} \cosh^{-2K}(\nu)
\end{align*}
\]

Consequently, the proof involves establishing the following identity:
\[
\cosh^{N}(\nu) \sum_{n=m}^{N} \sum_{K=m}^{n} \frac{N}{2n} \frac{K}{K} \frac{(-1)^{K-m-1}}{m+1} \cosh^{-2K}(\nu)
\]

For \( N \geq 2m \)
\[
\begin{align*}
&= \frac{N}{m^2} \sum_{n=m}^{\left\lfloor N/2 \right\rfloor} \sum_{m-1}^{n-1} \frac{(N-n-1)(n-m)(N-n-m)}{(m-1)(n-m)} \cosh [(N-2n)\nu] \\
&\quad \cdot \left( 1 - \frac{1}{2} \delta_{n,N/2} \right)
\end{align*}
\]

Let:
\[
f(N,\nu,m) = \sum_{n=m}^{N/2} \sum_{K=m}^{n} \frac{N}{2n} \frac{K}{K} \frac{(-1)^{K-m-1}}{m+1} \cosh^{-2K}(\nu)
\]
Then:

\[ \sum_{n=m}^{[N/2]} \sum_{K=m}^{(N-n)} \binom{N}{K} \binom{n}{m-K} (-1)^{K-m-1} \cosh^{-2K}(v) \]

\[ = \frac{1}{2} \left( \coth(v) \frac{a}{\partial v} + 2m \right) f(N, v, m) \]

But by hypothesis (V-7) we have:

\[ f(N, m, v) = \left( \frac{N}{m} \cosh^{-N}(v) \right)^{[N/2]} \sum_{n=m}^{(n-1)} \binom{N-n-1}{m-1} \cosh^{[N-2n]v} \]

\[ \cdot (1 - \frac{1}{2} \delta_n, N/2) \]

Therefore:

\[ \sum_{n=m}^{[N/2]} \sum_{K=m}^{(N-n)} \binom{N}{K} \binom{n}{m-K} (-1)^{K-m-1} \cosh^{-2K}(v) \]  

\[ = \frac{1}{2} \left( \coth(v) \frac{a}{\partial v} + 2m \right) \left[ \frac{N}{m} \sech^{-N}(v) \right]^{[N/2]} \sum_{n=m}^{(n-1)} \binom{N-n-1}{m-1} \cosh^{[N-2n]v} \]

\[ \cdot \cosh^{[(N-2n)]v} (1 - \frac{1}{2} \delta_n, N/2) \]

\[ = \frac{N}{2m} \sech^{-N}(v) \left[ \frac{N}{m} \right]^{[N/2]} \sum_{n=m}^{(n-1)} \binom{N-n-1}{m-1} \{(N-2n) \coth(v) \}

\[ \cdot \sinh^{[(N-2n)]v} + (2m-N) \cosh^{[(N-2n)v]} \}(1 - \frac{1}{2} \delta_n, N/2) \]

Observe now that:

\[ \coth(v) \sinh^{[(N-2n)v]} = \frac{1}{2} \sum_{K=0}^{\infty} \left\{ e^{(N-2n-2K)v} + e^{(N-2n-2K-2)v} - e^{-(N-2n+2K+2)v} - e^{-(N-2n-2K)v} \right\} \]  

(V-11)

\[ = \begin{cases} 
\cosh^{[(N-2n)v]} + 2 \sum_{K=1}^{[N/2]-n} \cosh^{[(N-2n-2K)v]}(1 - \frac{1}{2} \delta_K[N/2]-n) \\
0 \quad (n=0) 
\end{cases} \]
Consequently equation (V-10) becomes:

\[ \sum_{n=m}^{[N/2]} \sum_{K=m}^{n} \frac{(N/2-n)}{K} \left( \frac{n}{m} \right) \frac{1}{(K-m)} (-1)^{n-m-1} \cosh^{-2K} \left( \nu \right) \]  

\[ \text{(V-12)} \]

\[ = \left( \frac{N}{m} \right) \text{sech}^{N} (\nu) \sum_{n=m}^{[N/2]} \sum_{K=1}^{n-1} \frac{1}{(m-1)} \frac{(N-n-1)}{(m-1)} (N-2n) \]

\[ \cdot \cosh \left[ (N-2n-2K) \nu \right] (1 - \frac{1}{2} \delta_{K,[N/2]-n}) - \frac{(n-1)}{(m-1)} \frac{(N-n-1)}{(m-1)} \]

\[ \cdot (n-m) \cosh \left[ (N-2n) \nu \right] (1 - \frac{1}{2} \delta_{n,N/2}) \]

\[ = \left( \frac{N}{m} \right) \text{sech}^{N} (\nu) \sum_{n=m+1}^{[N/2]} \sum_{K=m+1}^{n} \frac{1}{(m-1)} \frac{(N-K)}{(m-1)} (N-2K+2) \]

\[ - \frac{(n-1)}{(m-1)} \frac{(N-n-1)}{(m-1)} (n-m) \cosh \left[ (N-2n) \nu \right] (1 - \frac{1}{2} \delta_{n,N/2}) \]

since:

\[ \sum_{n=m}^{[N/2]} \sum_{K=1}^{n-1} \frac{(n-1)}{(m-1)} \frac{(N-n-1)}{(m-1)} (N-2n) \cosh \left[ (N-2n-2K) \nu \right] \]

\[ = \frac{1}{2} \delta_{K,[N/2]-n} \left( 1 - \frac{1}{2} \delta_{n,N/2} \right) \]

\[ = \sum_{n=m}^{[N/2]} \sum_{K=1}^{n-1} \frac{(n-1)}{(m-1)} \frac{(N-n-1)}{(m-1)} (N-2n) \cosh \left[ (N-2n-2K) \nu \right] \]

\[ \cdot \left( 1 - \frac{1}{2} \delta_{n,[N/2]-n} \right) \]

\[ = \frac{(m-1)}{(N-m-1)} \frac{(N-2m)}{(m-1)} \sum_{K=1}^{[N/2]-m} \cosh \left[ (N-2m-2K) \nu \right] \]

\[ \cdot (1 - \frac{1}{2} \delta_{K,[N/2]-m}) + \frac{(m-1)}{(N-m-2)} \frac{(N-2m-2)}{(m-1)} \]

\[ \cdot \sum_{K=1}^{[N/2]-m-1} \cosh \left[ (N-2m-2K-2) \nu \right] \left( 1 - \frac{1}{2} \delta_{K,[N/2]-m-1} \right) + \ldots \]
\[
\begin{align*}
&= (m-1) \binom{N-m-1}{m-1} (N-2m) \sum_{K=m+1}^{[N/2]} \cosh [(N-2K)\nu] (1 - \frac{1}{2} \delta_{K,N/2}) \\
&+ (m-1) \binom{N-m-2}{m-1} (N-2m-2) \sum_{K=m+2}^{[N/2]} \cosh [(N-2K)\nu] (1 - \frac{1}{2} \delta_{K,N/2}) \\
&+ \ldots \\
&= \sum_{n=m+1}^{[N/2]} \sum_{k=m+1}^{n} (K-2) \binom{N-K}{m-1} \binom{N-2K+2}{m-1} \cosh [(N-2n)\nu] (1 - \frac{1}{2} \delta_{n,N/2}) \\
&= \left( \frac{N}{m} \right) \sum_{n=m}^{[N/2]} \sum_{K=m+1}^{N} (K-2) \binom{N-K}{m-1} \binom{N-2K+2}{m-1} \cosh [(N-2n)\nu] (1 - \frac{1}{2} \delta_{n,N/2}) \\
&= \left( \frac{N}{m} \right) \sum_{n=m}^{[N/2]} \binom{n-1}{m-1} \binom{N-n-1}{m-1} (n-m) \binom{N-n-m}{m-1} \cosh [(N-2n)\nu] (1 - \frac{1}{2} \delta_{n,N/2}) \\
\end{align*}
\]

To complete the proof by induction we must show (cf. equations (V-9) and (V-12) that:

\[
\sum_{n=m+1}^{[N/2]} \sum_{k=m+1}^{n} (K-2) \binom{N-K}{m-1} \binom{N-2K+2}{m-1} \cosh [(N-2n)\nu] (1 - \frac{1}{2} \delta_{n,N/2}) = 0
\]

Since \( \nu \) is arbitrary, the quantity in brackets must vanish so that the proof resolves itself into showing that:

\[
\sum_{K=m+1}^{N} (K-2) \binom{N-K}{m-1} \binom{N-2K+2}{m-1} = \frac{1}{m} \binom{n-1}{m-1} \binom{N-n-1}{m-1} (n-m) (N-m)
\]
which is equivalent to:
\[
\sum_{K=m+1}^{n} \left\{ \binom{K-2}{m-1} \binom{N-K+1}{m} - \binom{K-1}{m} \binom{N-K}{m-1} \right\} = \binom{n-1}{m} \binom{N-n}{m} \quad (V-14b)
\]

For \( m = 1 \) the proof is trivial:
\[
\sum_{K=2}^{n} (N-2K+2) = (n-1) (N-n)
\]

To investigate the general case one can expand the sum as follows:
\[
\binom{m-1}{m-1} \binom{N-m}{m} - \binom{m}{m} \binom{N-m-1}{m-1} + \binom{m}{m} \binom{N-m-1}{m} - \binom{m+1}{m} \binom{N-m-2}{m-1} + \binom{m+1}{m} \binom{N-m-2}{m} - \binom{m+2}{m} \binom{N-m-3}{m-1} + \cdots + \binom{n-3}{m-1} \binom{N-n+2}{m} - \binom{n-2}{m} \binom{N-n+1}{m-1} + \binom{n-2}{m} \binom{N-n+1}{m} - \binom{n-1}{m} \binom{N-n}{m-1}
\]

Observe now that
\[
\binom{r}{s} - \binom{r-1}{s-1} = \binom{r-1}{s} \quad (V-16)
\]

and
\[
\binom{r}{s} + \binom{r}{s-1} = \binom{r+1}{s}
\]

The proof of these two identities follows directly from the definition of the combinational symbol and is trivial. Using these identities one can combine the terms in the sum \((V-15)\) as follows:
\[
\binom{m-1}{m-1} \binom{N-m}{m} - \binom{m}{m} \binom{N-m-1}{m-1} = \binom{N-m-1}{m}
\]
\[
\binom{N-m-1}{m} \left[ \binom{m}{m} + \binom{m}{m-1} \right] = \binom{N-m-1}{m} \left( \binom{m}{m} + \binom{m}{m-1} \right)
\]
\[
\binom{m+1}{m} \left[ \binom{N-m-1}{m} - \binom{N-m-2}{m-1} \right] = \binom{m+1}{m} \binom{N-m-2}{m}
\]

Proceeding in this way we have finally:

\[
\begin{align*}
\binom{N-n+2}{m} & \left[ \binom{n-3}{m} + \binom{n-3}{m-1} \right] = \binom{n-2}{m} \binom{N-n+2}{m} \\
\binom{n-2}{m} & \left[ \binom{N-n+2}{m} - \binom{N-n+1}{m-1} \right] = \binom{n-2}{m} \binom{N-n+1}{m} \\
\binom{N-n+1}{m} & \left[ \binom{n-2}{m} + \binom{n-2}{m-1} \right] = \binom{n-1}{m} \binom{N-n+1}{m} \\
\binom{n-1}{m} & \left[ \binom{N-n+1}{m} - \binom{N-n}{m-1} \right] = \binom{n-1}{m} \binom{N-n}{m}
\end{align*}
\]

so that equation (v-14b) holds thus completing the proof by induction and proving the equivalence of the solution, equation (178) with the one-dimensional nearest-neighbor partition function obtained by a matrix method in Appendix IV.

The partition function, equation (221), can then be written as follows:

\[
Q = 2A \left\{ \cosh (N\nu) + \sum_{n=1}^{[N/2]} \frac{n}{n} \sum_{K=1}^{N} \binom{n}{K} \binom{N-n-1}{K-1} x_1^{-K} \right\} (v-17)
\]

\[
\times \cosh \left[ (N-2n)\nu \right] \left( 1 - \frac{1}{2} \delta_{n,N/2} \right)
\]

\[
= A \cosh^{N\nu} \left\{ (1 + \sqrt{1+W})^N + (1 - \sqrt{1+W})^N \right\}
\]

\[
W = (x_1^{-1} - 1) \sech^2 \nu
\]

\[
A = \begin{cases} 
\exp(N\nu) & \text{(Fluid)} \\
\exp(N\xi) & \text{(Ferromagnet)} 
\end{cases}
\]
APPENDIX VI

COMPUTER PROGRAM FOR A ONE-DIMENSIONAL FLUID WITH NEAREST-NEIGHBOR INTERACTIONS

The program in this appendix was used to evaluate the thermodynamic properties of a one-dimensional fluid with nearest-neighbor interactions from equations (308), (309), (310), (313), and (327).

The principal program variables and their counterparts in these equations are:

<table>
<thead>
<tr>
<th>Program Variables</th>
<th>Variable Name in the Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEPTH</td>
<td>z/k</td>
</tr>
<tr>
<td>RANGE</td>
<td>y</td>
</tr>
<tr>
<td>TEMP</td>
<td>T</td>
</tr>
<tr>
<td>Z</td>
<td>x₁⁻¹</td>
</tr>
<tr>
<td>W</td>
<td>W</td>
</tr>
<tr>
<td>S</td>
<td>√1+W</td>
</tr>
<tr>
<td>S₁</td>
<td>1+√1+W</td>
</tr>
<tr>
<td>U</td>
<td>v</td>
</tr>
<tr>
<td>Q</td>
<td>q=βpν</td>
</tr>
<tr>
<td>R</td>
<td>p</td>
</tr>
<tr>
<td>COMP</td>
<td>4kK_T/λ</td>
</tr>
<tr>
<td>CV</td>
<td>Cv/k</td>
</tr>
<tr>
<td>E</td>
<td>U</td>
</tr>
<tr>
<td>E₂</td>
<td>U_C</td>
</tr>
</tbody>
</table>
0056    76 FORMAT((6X, F8.2, 4X, F6.2, 6(4X, F14.7)))
0057    76 FORMAT((E8.2, 1X, E8.2, 1X, E(F14.7)))
0058        FNU
APPENDIX VII

COMPUTER PROGRAM FOR A FLUID WITH INFINITE-RANGE INTERACTIONS

The program in this appendix was used to compute the thermodynamic properties of a one-dimensional fluid with a potential well depth of $\zeta = 64k$ and range parameter $\gamma = 0$. Computations were made from equations (375), (376), (380), (381), and (384).

Variable names in the program and text are related as follows:

<table>
<thead>
<tr>
<th>Program Variables</th>
<th>Variable Name in the Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEPTH</td>
<td>$\zeta/k$</td>
</tr>
<tr>
<td>RANGE</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>TEMP</td>
<td>$T$</td>
</tr>
<tr>
<td>Z</td>
<td>$x_l^{-1}$</td>
</tr>
<tr>
<td>U</td>
<td>$v$</td>
</tr>
<tr>
<td>Q</td>
<td>$q = \beta p v$</td>
</tr>
<tr>
<td>D</td>
<td>$\rho$</td>
</tr>
<tr>
<td>COMP</td>
<td>$4kK_T$</td>
</tr>
<tr>
<td>CV</td>
<td>$C_v/k$</td>
</tr>
</tbody>
</table>
PROGRAM FOR PARTITION FUNCTION AND STATISTICS OF ONE-DIMENSIONAL SYSTEM OF PARTICLES WITH VERY LONG-RANGE INTERACTIONS

DIMENSION CF(500)

COSH(X) = (EXP(X) + EXP(-X))/2.
SINH(X) = (EXP(X) - EXP(-X))/2.
WRITE(3,72)
READ(1, 702) N
READ(1, 701) DEPTH, RANGE, TMIN1, TMIN2, TMAX1, TMAX2, TTNC1, TTNC2, TTNC3
READ(1, 701) UMIN1, UMIN2, UMAX1, UMAX2, UTNC1, UTNC2
AN2 = N/2.

IT1 = (TMIN2 - TMIN1) / TTNC1 + 0.5
IT2 = (TMAX1 - TMIN2) / TTNC2 + 0.5
IT3 = (TMAX2 - TMAX1) / TTNC3 + 0.5
IT = IT1 + IT2 + IT3 + 1
IU1 = (UMIN2 - UMIN1) / UTNC1 + 0.5
IU2 = (UMAX1 - UMIN2) / UTNC2 + 0.5
IU3 = (UMAX2 - UMAX1) / UTNC3 + 0.5
IU = IU1 + IU2 + IU3 + 1
WRITE(3, 76) IT, IU
DO 60 IT = 1, IT

402 IF(1 + IT - IT1) .GE. U02, 402, 403
TEMP = TMIN1 + (IT - 1) * TTNC1
GO TO 406
403 IF(IT1 - IT - IT2 + 1) .GE. U04, 404, 405
GO TO 406
404 TEMP = TMIN2 * (IT - IT1 - 1) * TTNC2
GO TO 406
405 TEMP = TMAX2 - (IT - IT1) * TTNC3
406 BJ = DEPTH / TEMP
Z = EXP(-BJ)
DO 60 IT = 1, IT
IF(2 * IU1 + IU2 + IU3 + 1) .GE. U08, 8, 9
IU = IU1 + IU2 + IU3 + 1
GO TO 801
8 IF(IT - IU1 - IU2) .GE. U10, 10, 11
IU = IU1 + IU2 + IU3 + 1
GO TO 801
11 U = TMAX2 - (2 * IU - IT2) * TTNC3
801 TN = 0.
TP1N = 0.
TP2N = 0.
TP4N = 0.
RN = 0.
RP1N = 0.
RP2N = 0.
CP2S = 1.
LMAX = N/2 + 1
DO 50 1 = 1, LMAX
51 L = 1
4 = L
IF(A - AN2) .GE. 12, 13, 12
H1 = 1.
GO TO 131
```plaintext
COPPEF=COMA*N*F7/H1
FCOSH=COSH(NLR*U)*COPPEF
FSINH=NLB*SINH(NLR*U)*COPPEF
LM2=LM1*L1M1
LM4=LM3*L1M1
TN=TN*FCOSH
TP2N=TP2N+LM2*FCOSH
TP3N=TP3N+LM3*FCOSH
TP4N=TP4N+LM4*FCOSH
RN=RN+FSINH
RP1N=RP1N+LM1*FSINH
RP2N=RP2N+LM2*FSINH
COMP=COMP*(N-2*TP2N/TN+4*TP2N/TN*N*PTNN*RTNN*N)/((N)*TDMP)
CV1=(N*TP2N+2*TP3N+TP4N/N)/TN
CV2A=(N*TP1N-TP2N)/TN
CV2=CV2A*CV2A/N
CV3A=(RP1N-RP2N*N-RTNN*N*TP1N-TP2N)
CV3B=RTNN-TP2N-N*RP1N+RP2N
CV3C=(N*(1-N)*RTNN-N*TP1N+TP2N)*4*TN
CV3=CV3A-CV3A/CV3C
CV=CV2A+AJ*AJ*(CV1-CV2+CV3)
WRITE(3,74) TEMP, L, QD, COMP, CV
GO TO 60
61601 WRITE(3,79) (CF(I), I=1, LNAX)
60 CONTINUE
100 CONTINUE
101 STOP
102 70 FORMAT(4X,9F7.2)
103 701 FORMAT(4X,8F7.2)
104 702 FORMAT(4X,14)
105 71 FORMAT(4X,N1=I,14.4X,DEPTH=I,F9,3,4X,IRANGE=F6.2)
106 72 FORMAT(14X,TEMP, I,QY,UI,12X,10I,17X,1D,15X,COMP,I,13X)
1 SPEC HC, T)
107 74 FORMAT(14X,F9.2,4X,F6.2,4AX,F14.7)
108 75 FORMAT(F6.2,1X,F6.2,1X,F6.2,4F14.7)
109 76 FORMAT(102X,14X,14)
110 77 FORMAT(10F14.7)
```
APPENDIX VIII

COMPUTER PROGRAM FOR FINITE SYSTEMS

The program in this appendix was used to compute the thermodynamic properties of finite systems. The systems analyzed were one-dimensional, two-dimensional, and three-dimensional. Equations used were those developed in Chapter VIII.

Program variables and variables in the text bear the following relationship to one another:

<table>
<thead>
<tr>
<th>Program Variable</th>
<th>Variable Name in the Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEPTH</td>
<td>ζ/k</td>
</tr>
<tr>
<td>RANGE</td>
<td>γ</td>
</tr>
<tr>
<td>V(L)</td>
<td>V_L/k</td>
</tr>
<tr>
<td>VI(L)</td>
<td>2φ_L/k</td>
</tr>
<tr>
<td>FT(L)</td>
<td>-2φ_L = 8θ_L</td>
</tr>
<tr>
<td>Z(L)</td>
<td>e^θ_L = X_L</td>
</tr>
<tr>
<td>PTNL1</td>
<td>2φ/k</td>
</tr>
<tr>
<td>PTNL</td>
<td>-βφ = 4θ</td>
</tr>
<tr>
<td>ZT</td>
<td>e^-βφ</td>
</tr>
<tr>
<td>U</td>
<td>ν</td>
</tr>
<tr>
<td>COMP</td>
<td>4kK_T/L</td>
</tr>
<tr>
<td>Q</td>
<td>q = βρν</td>
</tr>
<tr>
<td>D</td>
<td>ρ</td>
</tr>
<tr>
<td>CV</td>
<td>Cv/k</td>
</tr>
<tr>
<td>COR(L)</td>
<td>S_L</td>
</tr>
</tbody>
</table>
PROGRAM FOR PARTITION FUNCTION AND STATISTICS OF ONE-DIMENSIONAL SYSTEM OF PARTICLES

DIMENSION VI(25), TL(25), TF25), T(25), T0(25), TH(25), TE(25)
IV(25), COT(25), CI(25), FTC(25), DTC(25), IND(25), COP(25)

COS(Y)=EXP(Y)+EXP(-Y)/2.

WRITE (4, 72)
DO 1 I=1, 3
READ (1, 701) TDY, TIN1, TIN2, TMAX, TMAX2, TINC1, TINC2, TINC3
READ (1, 701) TDY, TIN1, TIN2, TMAX, TMAX2, TINC1, TINC2
WRITE (3, 71) N, DEPTH, RANGE
RTNL=0.
N=U/2.
TNL=1
Y(1)=-D(1)/U
N+1=1
Y(N)=V(N-1)+V(N)
401 RTNL=RTNL+1
DO 21 I=1, N
IV(I)=TDY+1+Y(I)
221 READ (25, 4) IV(I)
351 TMAX(TMAX)=TMAX+(TMAX-1)*TINC
352 TIN1(I)=TIN1(I)+TINC
353 TIN2(I)=TIN2(I)+TINC
354 TIN3(I)=TIN3(I)+TINC
355 T N=356
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496 T N=497
497 T N=498
498 T N=499
499 T N=500
500 T N=501
501 T N=502
502 T N=503
503
FORTRAN IV G LEVEL 6, M0000 MAIR DATE 147422 16/20/54

0054 TA=0.
0055 TP=0.
0056 TN=0.
0057 TF=0.
0058 0A=0.
0059 TN21=0.
0060 DC=0.
0061 DO. 802. I=1,N2
0062 IF(I-AM2)22.1.222.821
0064 N211=1.
0065 Gn TN 002
0066 p22 HN(1)=0.5.
0067 0o2 ECNP(1)=0.
0068 8=-1,0 MAX.
0069 Ln=1
0072 IF(A-AM2)12.13.14
0073 12 HN=1.
0074 Gn TN 131
0075 13 HN=0.5
0076 131 M1/N-2*1.0
0077 TL=7TE6[.8
0078 132 T1=6044ML+444441/7T1
0079 133 P1=10500ML+444441/7T1
0080 C1=M1*3/6+1
0081 T11=T1*1.00*1.0T1
0082 T12=T1*1.00*1.0T1
0083 U11=1.00*1.0T1
0084 T=1.
0085 TP2=0.
0086 DO 1211T=1,N2
0087 121 OT2((I)=0.
0089 14 1F((I-2))15.15.16
0090 16 T2=M
0091 Gd T0 40
0092 16 T2=0.
0093 DO 20 [I=1.I2
0094 H1(I)=1-I.
0095 20 M1(I)=N-1-I+1
0096 Gd TO((10.101.102.103.104.105.106.107.108).KL
0097 100 M1(4)=1
0097 101 M1(5)=1
0100 101 M1(6)=1
0101 102 M1(7)=1
0102 102 M1(8)=1
0103 103 M1(7)=1
0104 103 M1(8)=1
0105 104 M1(7)=1
0106 104 M1(8)=1
0107
0222 702 FORMAT(AV, 14)
0223 71 FORMAT(//AY, 1M=1, 14, 4X, IDENT=2, 2X, ER, 2, 4X, FR, 2, 4X, EA, 2, 1X, 4, 1X, 4, 14, 7)
0224 72 FORMAT(AY, 1M=1, 14, 4X, IDENT=2, 2X, ER, 2, 4X, FR, 2, 1X, 4, 1X, 4, 14, 7)
0225 73 FORMAT(AY, 1M=1, 14, 4X, 14)
0226 74 FORMAT(AY, 1M=1, 14, 4X, 14)
0227 75 FORMAT(AY, 1M=1, 14, 7)
0228 76 FORMAT(AY, 1M=1, 14, 7)
0229 77 FORMAT(AY, 1M=1, 14, 7)
0230 78 FORMAT(AY, 1M=1, 14, 7)
0231 79 FORMAT(AY, 1M=1, 14, 7)
0232 80 FORMAT(AY, 1M=1, 14, 7)
0233 81 FORMAT(AY, 1M=1, 14, 7)
0234 82 FORMAT(AY, 1M=1, 14, 7)
0235 83 FORMAT(AY, 1M=1, 14, 7)
0236 84 FORMAT(AY, 1M=1, 14, 7)
0237 85 FORMAT(AY, 1M=1, 14, 7)
0238 86 FORMAT(AY, 1M=1, 14, 7)
0239 87 FORMAT(AY, 1M=1, 14, 7)
END
VITA

The author was born on 17 January 1923 in Germany and started his schooling in that country. He completed his secondary education at Lake View High School in Chicago. After two years of undergraduate work at the University of Chicago he was called to military service in July 1943. He was commissioned a second lieutenant in the U.S. Army in January 1945, accepted a commission in the regular army of the United States after World War II and served in a variety of assignments of increasing responsibility in various parts of the world until his retirement from active military service in September 1964 in the rank of Lieutenant Colonel, Corps of Engineers. He holds the following degrees: B.S., Economics, Sophia University, Tokyo, Japan, 1952; B.S. Civil Engineering, Missouri School of Mines and Metallurgy, Rolla, Missouri, 1959; M.S., Physics, University of Missouri at Rolla, 1966. He is a Registered Professional Engineer in the State of Missouri. During his residence in the Graduate School of the University of Missouri he held as NASA Predoctoral Traineeship and later an appointment as Instructor in the Mathematics Department. He is married to the former Alison Squire and has two sons, Michael and Anthony, 15 and 10 years old respectively.