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THE STATISTICS OF FINITE, ONE DIMENSIONAL LATTICE FLUIDS

by

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A DISSERTATION

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In Partial Fulfillment of the Requirements for the Degree

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in

PHYSICS

1969

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ABSTRACT

A one dimensional lattice fluid in which particles are allowed to assume only discrete positions is proposed. Particles are free to move from one lattice site to another interacting through a variety of potentials, including the Lennard-Jones type. The model allows the partition function to be evaluated as a discrete sum over the allowable configurations. Both the canonical ensemble and grand ensemble are treated by computer and a third, the pressure ensemble, is considered and shown to be useful in the theoretical treatment of lattice systems. The thermodynamic behavior of various systems is investigated in both the canonical and grand ensembles. Both ensembles reveal that low temperature behavior of a system is distinctly different than that observed at high temperatures although there is not exact agreement between the two results.

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I wish to express my sincere appreciation to Dr. Louis H. Lund for suggesting the problem and for his keen interest and many helpful discussions. I also wish to express my gratitude to my wife Carolyn for her patience and encouragement during my research.

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INTRODUCTION

One of the most difficult and for the most part still unsolved problems of theoretical physics is the calculation of the thermodynamic properties of fluid systems. Only a small number of problems have been solved exactly. The one and two dimensional Ising model solutions stand out as one of the few exactly solved systems where transitional phenomena are observed[1]. As is well known, the difficulty arises from the large numbers of particles involved and the lack of a real understanding of the interparticle interactions. For gaseous low-density systems, one can often obtain power series approximations such as the Mayer cluster expansions[2]. Such expansions in powers of the density give reasonable answers for low density systems since one must keep only the first few terms which are relatively easy to calculate. For solid systems where the density is large, one can take advantage of periodicity and high symmetry to allow one to reduce the complexity to the point where one can make rational, semi-empirical approximations and obtain valuable results to explain many phenomena. The liquid system cannot be attacked by either technique. Its density is too large for cluster expansions to be of use and there is not sufficient symmetry to utilize the approximations which work in the case of solids.

While the two dimensional Ising model exhibits a phase transition, the one dimensional model does not. Nevertheless, the simplicity of the model and the availability of computer machinery make it, or rather generalizations of it, attractive since one can set up programs to compute thermodynamic properties by machine. The ease of the computation together with the remarkably realistic nature of the results and the relatively simple interpretation of the data which one obtains from the computer calculations make this an appealing investigation.

In recent years the primary route of attack has been the attempt to calculate the pair distribution function and to compute thermodynamic properties from this. One elegant route is the use of the Kirkwood-superposition approximation[3]. This approach leads to an integral equation to be solved for the pair distribution function. Approximations in turn must be made to solve the integral equations. With this series of approximations and simplifications the physical system of interest is only remotely akin to the theoretical predictions. Nevertheless, such work has been useful in obtaining a qualitative idea of the nature of a liquid and what happens when a low density system undergoes a change in phase.

In order to approximate physical systems, one must treat extremely large numbers of particles, and it has been shown that the discontinuous behavior of the thermodynamic quantities one observes experimentally can only be obtained in the limit of large systems, namely where the number of particles becomes infinite while the volume per particle or particle density remains fixed[4]. Actually, the "sudden" changes characteristic of transitional phenomena are observed in finite real systems and can be explained by noting that the number of particles involved is quite large, on the order of 10^{23}, so that even though changes are not truly discontinuous the region over which the changes occur is so small no measuring apparatus is capable of measuring it. However, changes which do not qualify as true phase transitions can occur in finite and even small systems. Consider, for example, water in a glass. If one views it for a short time, it appears to be in a stable state and yet if left to stand the water will eventually evaporate and thus is not truly in a stable state. Fluids can present phases other than the gaseous state which will persist for long times compared to usual time standards, but not be a truly stable phase in the sense that this is the only state the system can be in. It thus appears as though it depends upon when one examines a system as to what phase he ascribes to it or, in other words, these cannot be true equilibrium states but are mere metastable states. Time dependent theory is not yet in a completely satisfactory state and so we shall be content to look at equilibrium statistics. We shall look at finite systems to see if any behavior can be observed which would suggest a phase transition or at least the existence of relatively ordered stable states which occur with large enough probabilities to affect the behavior of the thermodynamic functions to the point that a phase change may be anticipated.

One wishes to treat problems exactly and in complete generality with regard to potential interaction in order to concentrate on the physical problem instead of the mathematical one and the model we have chosen allows us to do just that.

Some of the motivation for this work was provided by the success of the work of Ralph G. Tross[5], who investigated this problem and who employed the University of Missouri -- Rolla computer to study finite systems of particles interacting through a modified Lennard-Jones potential[5]. In this study, we go beyond this. We look at a variety of potentials and systems investigating the thermodynamics. Tross used a computation method which restricted his study to systems in which particle size is identical to lattice size and consequently his data is somewhat biased by this coincidence. His correlation function data show none of the local maxima and minima associated with this function in the continuum. Since particle size is identical to lattice size, only separations of an integral number of particle diameters can occur. This means that no effects show up which correspond to the case where two particles are separated by 1½ diameters, for example. For this case, a total length of 2½ particle diameters is excluded from occupancy by other particles, whereas at a separation of 2 particle diamters only 2 particle diameters is excluded. Thus correlation at a separation of 2 diameters should be larger than that at 1½ diameters or for 2½, etc. This shows that the local maxima occur in the neighborhood of separations of integral numbers of particle diameters. We show herein that by considering systems where particle size and lattice size differ, we obtain data more closely in line with observed phenomena. We also expose some of the peculiarities of our model by considering the low temperature behavior of our system particularly with regard to pressure.

CHAPTER II

MATHEMATICAL FORMULATION

A. Introduction to the Model

We wish to consider a one dimensional system containing n particles and having a volume (length) L. In any finite system, the boundaries play an important role in the physical behavior (if this were not true, removal of the boundaries would produce little effect). The type of boundary condition we shall consider is the so-called periodic boundary condition. We choose the periodic boundary condition because certain aspects of such systems result in simplifications that mean reduced computer time. We assume that the system of interest is imbedded in an infinite number of identical systems which are exact copies of the system of interest. We assume that the real system is located from 0 to L along the line and that the copies lie alongside going to the left from 0 → -L, -L → -2L, -2L → -3L, etc., and to the right from L → 2L, 2L → 3L, etc., as shown in Figure 1.

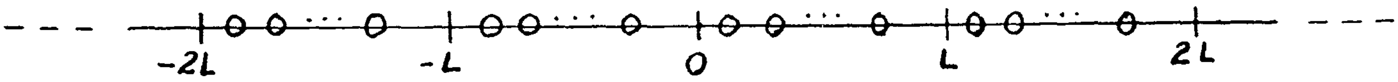


Figure 1. Periodic Boundary Conditions

We assume that particles only interact with others that are closer than L units away. Note that as a particle leaves the system at L another identical to it enters at 0.

Let us leave our consideration of the boundary conditions for a moment and consider the statistics. We choose to employ the formalism of the canonical ensemble turning later to a look at the grand ensemble. We compute the canonical ensemble partition function $Q_n(V,\beta)$ of a system of n particles volume V and temperature $1/k\beta$ as follows[6]. We let p and q represent collectively the position and momentum coordinates of the particles.

$$Q_n = \frac{1}{n!\,h^n} \underset{\left(\substack{\text{configuration}\\ \text{space}\\ V}\right)}{\int dq} \; \underset{\left(\substack{\text{momentum}\\ \text{space}}\right)}{\int dp} \; e^{-\beta H(p,q)} \tag{1}$$

In most systems the interparticle interaction depends only on the positions of the pair of interacting particles and the total interaction is the sum of all pairwise interactions. We can thus write the Hamiltonian H(p,q) as the sum of the kinetic energy term plus the total potential interaction energy

$$H(p,q) = \sum_{i=1}^{n} \frac{p_i^2}{2m} + \sum_{1\le i<j\le n} V(q_i,q_j) \tag{2}$$

p_i is the momentum of the ith particle, m is the mass of a particle and $V(q_i,q_j)$ is the binary interaction potential.

In this form it is apparent that the momentum space integral in Equation (1) can be performed independently of the configuration integral. Thus we perform the momentum integral so that our problem becomes one of evaluating the configuration integral. We can rewrite (1) now as

$$Q_n(V,\beta) = \frac{1}{n!}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{n}{2}} \int\limits_{\left(\substack{\text{config.}\\ \text{space}\\ V}\right)} dq\; e^{-\beta U(q)} \tag{3}$$

For convenience, let us collect the configuration integral into one unit and call it $C_n(V,\beta)$.

$$C_n(V,\beta) = \frac{1}{n!}\int\limits_{\left(\substack{\text{config}\\ \text{space}\\ V}\right)} dq\; e^{-\beta U(q)} = \frac{1}{n!}\int_0^L\int_0^L\cdots\int_0^L dq_1\cdots dq_n\; e^{-\beta U(q_1\cdots q_n)} \tag{4}$$

One has little or no hope of being able to evaluate the integral in Equation (4) in most instances and this is the crux of the problems in statistical mechanics. To get around this difficulty, we reshape the problem in order to cast the integral above into a form suitable for computer evaluation. We do this by making the linear system into a lattice of discrete points with lattice parameter ℓ such that $L = N\ell$ with N an integer. We locate our lattice sites at $\ell/2$, $3\ell/2$, $5\ell/2$, $\cdots$, $(2N-1)\ell/2$. To agree with convention we call the segment of length ℓ which has a lattice site at its center a cell. Thus cell 1 lies from 0 to ℓ, cell 2 from ℓ to 2ℓ, $\cdots$, cell N from $(N-1)\ell$ to $N\ell$. We now make the further assumption that when a particle lies in a cell, the effects of that particle are as if it were located at the center of the cell on the site there. Thus, effectively, only discrete positions can be assumed by a particle. With this new picture we define an appropriate parameter cell occupancy. We label the cells 1, 2, 3, $\cdots$, N, N+1, N+2, $\cdots$, recalling the periodic copies of this system. Let σ_j be the occupancy of cell j. With this definition now we can picture the total interaction as a sum of interactions between cells. The interaction between cells i and j would be $\sigma_i\sigma_j\ V((i - 1/2)\ell,(j - 1/2)\ell)$.

The potentials we shall be using are of the hard core, spherically symmetric type. That is, we assume $V(q_i,q_j) = V(|q_i - q_j|)$ and further $V(r) = \infty$ if $r < d$ where d is the particle diameter. In our lattice system, no pair of particles can be more than $(N-1)\ell$ units apart. Now there are only N possible values of the separation and hence let us examine the possibility that it might be useful to represent the interaction potential as a sum over the various particle separations as follows:

$$U(q_1 \cdots q_n) = \sum_{j=0}^{N-1} P_j\ V(j\ell) \tag{5}$$

P_j is just the number of pairs of particles separated by the distance $j\ell$. Because we have assumed the hard core form of potential no cell can be occupied by more than one particle. Also, no two particles can be closer than d. If $d > \ell$, this means that the "excluded" space around a particle is more than one cell.

From the preceding discussion, we can write

$$P_j = \sum_{k=1}^{N} \sigma_k \sigma_{k+j} \tag{6}$$

In Equation (6) we note that for some values of the summation index k, k + j exceeds N. From the periodic boundary conditions we can replace such a value by

$$\sigma_{k+j} = \sigma_{k+j-N} \tag{7}$$

With this, then, we have a complete description of the system. For convenience let $V_j = V(j\ell)$.

Let us collect the results of the previous discussion

$$U = \sum_{j=1}^{N-1} P_j V_j = \sum_{j=1}^{N-1} \sum_{k=1}^{N} \sigma_k \sigma_{k+j} V_j \tag{8}$$

The set of quantities $\{P_j\}$ is a convenient artifice for computing the energy U. Let us form a vector from this set and call it the profile or profile vector with jth component P_j. Equation (8) can be rewritten in such a way as to show that the profile is actually a sum of two parts.

$$U = \sum_{j=1}^{N-1} V_j \left[\sum_{k=1}^{N-j} \sigma_k \sigma_{k+j} + \sum_{k=N-j+1}^{N} \sigma_k \sigma_{k+j} \right]$$

$$= \sum_{j=1}^{N-1} V_j \left[\sum_{k=1}^{N-j} \sigma_k \sigma_{k+j} + \sum_{k=1}^{j=N-(N-j)} \sigma_k \sigma_{k+N-j} \right]$$

$$U = \sum_{j=1}^{N-1} V_j \left[\mathcal{P}_j + \mathcal{P}_{N-j} \right] \quad \text{thus} \quad P_j = \mathcal{P}_j + \mathcal{P}_{N-j} \tag{9}$$

$$\mathcal{P}_j = \sum_{k=1}^{N-j} \sigma_k \sigma_{k+j} \tag{10}$$

Equation (9) can be cast in a different form

$$U = \sum_{j=1}^{N-1} V_j \mathcal{P}_j + \sum_{j=1}^{N-1} V_j \mathcal{P}_{N-j} = \sum_{j=1}^{N-1} V_j \mathcal{P}_j + \sum_{j=1}^{N-1} V_{N-j} \mathcal{P}_j$$

$$U = \sum_{j=1}^{N-1} \mathcal{P}_j \left(V_j + V_{N-j} \right) \tag{11}$$

We can now discuss the topology of the periodic system. This is established by first noting that as a particle leaves at one end, another enters at the other end so that there are always n particles in the system. Further suppose we move the origin a distance x lattice constants to the right. Under such a transformation, none of the relative separations is changed and since the energy of interaction depends only on relative separation, it remains fixed under this translation. This demonstrates that the periodic boundary conditions give the finite system the transational properties of the infinite lattice. This also implies that our system has the topological properties of the circle with cell N immediately adjacent cell 1 as shown in Figure 2.

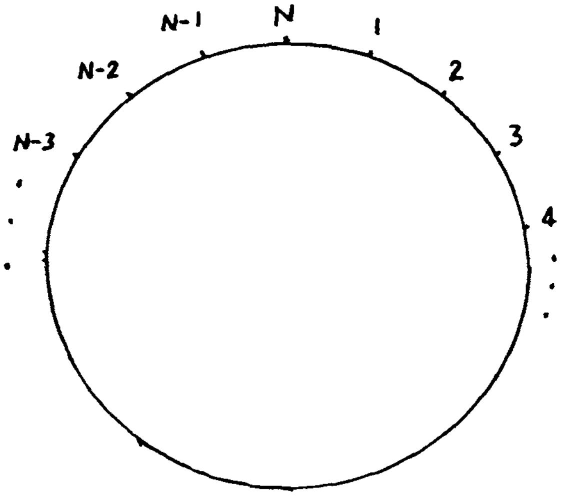


Figure 2. Topology of Periodic System

Recall Equation (11). The quantity p_j is the jth component of the profile for a system in which no particle lies beyond L, as in the periodic system. Hence, it looks as if the interaction between a pair of particles separated by $j\ell$ consists of an interaction around each limb of the circle as $V(j\ell) + V(L-j\ell) = V_j + V_{N-j}$.

Let us now return to the profile $P = (P_j)$ and examine it more closely to see what symmetries it has. First, as we stated earlier, P is independent of where we place the origin or equivalently is invariant under lattice translations as shown by the following. We assume that the new configuration is given by

$$\sigma_j' = \sigma_{j+r} \tag{12}$$

from which $P_j' = \sum_{k=1}^{N} \sigma_k' \sigma_{k+j}' = \sum_{k=1}^{N} \sigma_{k+r}\, \sigma_{k+r+j}$

$$P_j' = \sum_{k=1+r}^{N+r} \sigma_k\, \sigma_{k+j} = \sum_{k=1+r}^{N} \sigma_k\, \sigma_{k+r} + \sum_{k=1}^{r} \sigma_{k+N} \sigma_{k+j+N}$$

The periodicity of the lattice implies that $\sigma_{k+N} = \sigma_k$

$$\Longrightarrow P_j' = \sum_{k=1+r}^{N} \sigma_k\, \sigma_{k+j} + \sum_{k=1}^{r} \sigma_k\, \sigma_{k+j} = P_j \tag{13}$$

This result confirms the assertion made earlier that the lattice has translational symmetry and that the energy $U' = \sum_{j=1}^{N} P_j' V_j = \sum_{j=1}^{N} P_j V_j = U$. It is clear also that relative locations and interactions do not depend on the "handedness" of the coordinate system so that an exchange of left for right handed coordinates does not change the relative separation; thus, the transformation $\sigma_j' = \sigma_{N-j+1}$ leaves the energy invariant.

B. Theoretical Development

(1) Canonical Ensemble

The degeneracy of the potential energy U due to lattice symmetry and completely independent of any assumed potential has been observed. There is complete translation symmetry and symmetry in the exchange of left handed for right handed reference frames. These results were obtained independent of the potential to show their completely general nature.

As stated previously, potentials of the hard core type are assumed with hard core diameter d. It is also assumed that d can be written as an integral number of lattice constants so that $d = e\ell$. If the particle diameter is just equal to the lattice constant ℓ so that $e = 1$, then the cell occupancy number σ_j satisfies an exclusion principle, in that σ_j can only be 0 or 1 but occupancy of cell j does not preclude occupancy of cell $j + 1$. It is this nature of the special case $d = \ell$ which was attractive in earlier formulations. It is but a special case of the more general problem we treat for if

$d = 2\ell$ or 3ℓ, etc., occupancy of j prohibits occupancy of j + 1. If $d = e\ell$, then occupancy of j precludes occupancy of $j+1, j+2, \cdots, j+e-1$. As a simple convention we assign a particle to the cell in which its left edge lies so that even though a particle actually fills e cells it is assigned to a single cell.

The lattice concept introduces some quantum features into this classical problem as a result of the uncertainty of position of a particle ℓ. In other words, if a particle lies in a cell its position is taken as the center of the cell and if it should lie on a cell boundary it is assigned to the cell to its left. Since we desire to treat systems where $e > 1$, we renew our search for a convenient representation.

Cell occupancy is convenient only when $e = 1$ so that the quantities σ_j are completely independent except for the requirement that the system contains n particles.

$$\sum_{j=1}^{N} \sigma_j = n \tag{14}$$

When $e \geq 2$, Equation (14) must still hold but now $\sigma_1 = 1 \Rightarrow \sigma_2, \sigma_3, \cdots, \sigma_{e-1} = 0$ and hence the σ's are no longer independent. We now set out to find an alternative representation in which the problem can be stated and formulated.

To determine the interaction energy, it is but necessary to determine the set of values $(p_1, p_2, \cdots, p_{N-1})$. For a finite number of particles we note that $\lim_{N\to\infty} P_j = p_j$. For this reason we refer to p_j as the infinite profile.

When e = 1 it is possible to show a 1 - 1 correspondence between configurations of n particles in N cells and N - n particles in N cells. One merely needs to make the transformation

$$\sigma_j' = 1 - \sigma_j \tag{15}$$

to see this fact. The energy of the corresponding configuration is related to the original as follows

$$U' = \sum_{j=1}^{N-1} P_j' V_j = \sum_{j=1}^{N-1} V_j \left(\sum_{k=1}^{N} \sigma_k' \sigma_{k+j}' \right)$$

$$= \sum_{j=1}^{N-1} V_j \sum_{k=1}^{N} (1-\sigma_k)(1-\sigma_{k+j})$$

$$\begin{aligned} U' &= \sum_{j=1}^{N-1} V_j (N-2n+P_j) \\ &= (N-2n) \sum_{j=1}^{N-1} V_j + U \end{aligned} \tag{16}$$

The cell occupancy number representation is an appealing one because of the pseudo-quantum nature of the problem but it ceases to be useful so we must forget it. Suppose we write the values of cell occupancy number down as a finite sequence of N elements all 0's or 1's.

$$[00\cdots01010\cdots010\cdots0] \tag{17}$$

An arbitrary configuration would resemble Equation (17) in appearance. This suggests another representation to us; namely, suppose we call a_j the number of free cells between the jth and j+1st particles. By free cell, we mean a cell which is not occupied and is not covered by a particle in a nearby cell. For e = 1 we merely count the zeros between j and j+1 to find a_j. If $e \neq 1$, we ignore those cells covered by a particle and count only those left. Before, we could represent every possible arrangement of particles by merely specifying the values of the σ's to correspond to the filled and empty cells. We shall show later that the partition function or at least the configuration integral is the result obtained by summing overall allowed configurations of particles in the cells. The representation in terms of the a's is not 1 - 1 to that in terms of σ's as the following example shows. Consider the configuration [10110] of 3 particles in 5 cells. The corresponding a's are $a_1 = 1$, $a_2 = 0$. $(e = 1)$ Also for [01011] $a_1 = 1$, $a_2 = 0$ so that two configurations of the system correspond to the same "a" representation. Both configurations have the same profile since the second is a translation of the first so that the a's are a somewhat smaller set of coordinates, i.e., they represent fewer distinct cases than the σ's (a desirable property).

The quantity a_j is actually related to the separations of particles j and j+1 as

$$a_j = \frac{q_{j+1} - q_j}{\ell} - e \tag{18}$$

Thus the set of quantites a_j must be viewed as having arisen from the representation in which particle position is the fundamental variable. The possible positions a particle can occupy are $\ell/2$, $3\ell/2$, $5\ell/2$, $\cdots$, $(2N-1)\ell/2$. For convenience, we now define a new set of position coordinates in which the lattice spacing is unity and the coordinate takes on only integral values.

$$X_j = q_j/\ell + 1/2 \tag{19}$$

Returning for a moment to the continuum, we recall the configuration integral from Equation (3).

$$C_n(L,\beta) = \frac{1}{n!} \int_0^L \int_0^L \cdots \int_0^L dq_1 \cdots dq_n \; e^{-\beta U(q_1 \cdots q_n)} \tag{3}$$

If we make the transformation from the q's to the x's, we have

$$C_n(L,\beta) = \frac{\ell^n}{n!} \int_{1/2}^{\frac{L}{\ell}+\frac{1}{2}} \int_{1/2}^{\frac{L}{\ell}+\frac{1}{2}} \cdots \int_{1/2}^{\frac{L}{\ell}+\frac{1}{2}} dx_1 \cdots dx_n \; e^{-\beta U(x_1 \cdots x_n)} \tag{20}$$

We now wish to express this result in a form appropriate to our lattice

$$C_n(L,\beta) = \frac{\ell^n}{n!} \sum_{x_1=1}^{N} \sum_{x_2=1}^{N} \cdots \sum_{x_n=1}^{N} \Delta x_1 \, \Delta x_2 \cdots \Delta x_n \; e^{-\beta U(x_1 \cdots x_n)} \tag{21}$$

In the x variables the cell size is unity so that $\Delta x_i = 1$ and hence 21 becomes

$$C_n(L,\beta) = \frac{\ell^n}{n!} \sum_{x_1=1}^{N} \cdots \sum_{x_n=1}^{N} e^{-\beta U(x_1 \cdots x_n)} \tag{21'}$$

We do not stop here, however, because we can reduce this form further to eliminate the repetitious terms in Equation (21'). It is true that in any system of identical particles we can interchange any pair without changing the total interaction energy at all. This means that we can separate the sums in Equation (21) into parts in each of which the particles are in a definite order. We can take any term in any one of the parts and make it a term in any other by interchanging particles judiciously. Thus each part will have the same value as the others, meaning that we need keep only one and multiply it by the number of different parts. There is a different part for each order in which the particles could be placed. Since there are n particles, there are n! permutations of n things n at a time, hence n! parts

$$C_n(L,\beta) = \frac{\ell^n}{n!}\Big[n! \underset{x_1 < x_2 < \cdots < x_n}{\sum_{x_1=1}^{N} \sum_{x_2=1}^{N} \cdots \sum_{x_n=1}^{N}} e^{-\beta U(x_1 \cdots x_n)} \tag{21''}$$

Every order of the particles will produce the same result so we choose to keep the particles in numerical order. In addition to this, the hard-core diameter e (in units of ℓ) means, for example, $x_1 + e \leq x_2$, $x_2 + e \leq x_3$, $\cdots$, $x_{n-1} + e \leq x_n$, $x_n + e \leq x_1 + N$. With these ideas in mind, we take another look at our task.

The sum in Equation (21") indicates that we must set up our summation apparatus so that order is preserved, particles never come closer than e cells to one another, and all possible configurations are reached. To accomplish this we consider the possibilities. First, if $x_1 = 1$, we note from the above that $x_n \leq N + x_1 - e = N + 1 - e$. This of course limits the other particles as well since they must lie between x_1 and x_n. We construct the following table

$$\begin{aligned} X_1 + e &\leq X_2 \\ X_2 + e &\leq X_3 \\ X_3 + e &\leq X_4 \\ &\vdots \\ X_{n-1} + e &\leq X_n \\ X_n + e &\leq X_1 + N \quad \text{also} \quad X_n \leq N \end{aligned} \tag{22}$$

We generate all configurations by allowing x_1 to take on all possible values $x_1 = 1, 2, 3, \cdots, N - ne + e$. With these considerations we write down the configuration integral.

$$\begin{aligned} C_n(L, \beta) = \ell^n \Bigg[& \underset{(X_1 = 1)}{\sum_{X_2 = 1+e}^{N+1-(n-1)e} \sum_{X_3 = X_2+e}^{N+1-(n-2)e}} \cdots \sum_{X_n = X_{n-1}+e}^{N+1-e} \\ & + \underset{(X_1 = 2)}{\sum_{X_2 = 2+e}^{N+2-(n-1)e} \sum_{X_3 = X_2+e}^{N+2-(n-2)e}} \cdots \sum_{X_n = X_{n-1}+e}^{N+2-e} \\ & + \cdots + \underset{(X_1 \geq e)}{\sum_{X_1 = e}^{N+e-ne} \sum_{X_2 = X_1+e}^{N+e-(n-1)e}} \cdots \sum_{X_n = X_{n-1}+e}^{N+e-e} \Bigg] e^{-\beta U(X_1 \cdots X_n)} \end{aligned} \tag{23}$$

Let us now turn to the evaluation of the interaction energy in terms of particle positions.

$$U(x_i) = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \left[V(x_j - x_i) + V(N - (x_j - x_i)) \right] \tag{24}$$

The sum in Equation (24) runs over all distinct pairs of particles, summing the pairwise interactions under the assumption that the interaction between 2 particles consists of an interaction around each limb of the circle. For convenience, we define a pseudo-Kronecker delta function.

$$\delta(X) = \begin{matrix} 0 & ; & X \neq 0 \\ 1 & ; & X = 0 \end{matrix} \tag{25}$$

Using this definition, we can rewrite $U(x_1 \cdots x_n)$ as

$$U(x_1 \cdots x_n) = \sum_{\ell=1}^{N-1} (V_\ell + V_{N-\ell}) \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \delta(\ell - (x_j - x_i)). \tag{26}$$

To show that this is equivalent to our previous form, we note that the cell occupancy number can be expressed as a function of position coordinates.

$$\sigma_m = \sum_{\ell=1}^{n} \delta(m - x_\ell) \tag{27}$$

We shall show with the aid of (27) that the double sum over i and j is equal to the infinite profile p_ℓ.

$$p_\ell = \sum_{k=1}^{N-\ell} \sigma_k \, \sigma_{k+\ell} = \sum_{k=1}^{N-\ell} \sum_{i=1}^{n} \sum_{j=1}^{n} \delta(k - x_i)\, \delta(k + \ell - x_j)$$

By the nature of the problem $x_i \leq N$ so that if $x_j - x_i = \ell$ then both δ-functions cannot be simultaneously nonzero if $k > N - \ell$. This means that we can extend the sum to N so that

$$\begin{aligned} p_\ell &= \sum_{k=1}^{N} \sum_{i=1}^{n} \sum_{j=1}^{n} \delta(k - x_i)\, \delta(k + \ell - x_j) \\ &= \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{N} \delta(k - x_i)\, \delta(k + \ell - x_j) \end{aligned}$$

$$p_\ell = \sum_{i=1}^{n} \sum_{j=1}^{n} \delta(x_i + \ell - x_j) \tag{28}$$

The only nonzero terms in Equation (28) are those terms for which $x_j - x_i = \ell$. In order for x_j to exceed x_i, j must exceed i since we previously ordered the particles numerically. Hence we can ignore those terms in (28) for which $j \leq i$. Then we have

$$P_\ell = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \delta(x_i - x_j + \ell) = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \delta(\ell - (x_j - x_i)) \tag{29}$$

With this result we can rewrite (26)

$$U(x_1 \cdots x_n) = \sum_{\ell=1}^{N-1} (V_\ell + V_{N-\ell}) P_\ell \tag{26'}$$

This result agrees with Equation (11) demonstrating that these two approaches lead to the same energy as they must. We must use this result to compute the energy for the position representation.

Let us start with Equation (23) and make the substitution in favor of the a_j's defined previously

$$a_j = x_{j+1} - x_j - e \tag{30}$$

We can express the x's in terms of the a's and x_1 as follows:

$$x_j = x_1 + \sum_{i=1}^{j-1}(a_i+e) = x_1 + \sum_{i=1}^{j-1} a_i + (j-1)e \tag{31}$$

$$C_n(L,\beta) = \ell^n\Big[\sum_{a_1=0}^{N-ne}\ \sum_{a_2=0}^{N-ne-a_1}\ \sum_{a_3=0}^{N-ne-a_1-a_2}\cdots\sum_{a_n=0}^{N-ne-\sum_{j=1}^{n-2}a_j} + \cdots$$

$$+ \sum_{a_1=0}^{N-ne}\ \sum_{a_2=0}^{N-ne-a_1}\ \sum_{a_3=0}^{N-ne-a_1-a_2}\cdots\sum_{a_{n-1}=0}^{N-ne-\sum_{j=1}^{n-2}a_j}$$

$$+ \sum_{x_1=e}^{N-ne+e}\ \sum_{a_1=0}^{N-ne+e-x_1}\ \sum_{a_2=0}^{N-ne+e-x_1-a_1}\cdots\sum_{a_{n-1}=0}^{N-ne+e-x_1-\sum_{j=1}^{n-2}a_j}\Big]e^{-\beta\,U(x_1\cdots x_n)} \tag{32}$$

Since we have expressed the x's in terms of the a's, we can now rewrite $u(x_1 \cdots x_n)$ as a function of the a's

$$U(x_1\cdots x_n) = U(a_1\cdots a_{n-1})$$

$$= \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\Big[V\Big(\sum_{k=i}^{j-1}(a_i+e)\Big) + V\Big(N-\sum_{k=i}^{j-1}(a_i+e)\Big)\Big]$$

In this last form we notice that the energy u no longer depends on the coordinate x_1 indicating the fact that energy of interaction depends only on interparticle separations and not absolute locations. This means that we can rid ourselves of the sum over x_1 and reduce our work thereby. This requires that we interchange the order of summation until the sums over x_1 are innermost. We do this pairwise, that is, we interchange summations in a pairwise manner until the sum over x_1 is inside. Since the energy does not depend on x_1, we can change this variable by reducing it so that the sum on x_1 starts at zero. For convenience let $F = N - ne$.

$$C_n(L,\beta) = \ell^n\Big[\sum_{a_1=0}^{F}\sum_{a_2=0}^{F-a_1}\cdots\sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j} + \cdots + \sum_{a_1=0}^{F}\sum_{a_2=0}^{F-a_1}\cdots\sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j}$$
$$+ \sum_{x_1=0}^{F}\sum_{a_1=0}^{F-x_1}\sum_{a_2=0}^{F-x_1-a_1}\cdots\sum_{a_{n-1}=0}^{F-x_1-\sum_{j=1}^{n-2}a_j}\Big] e^{-\beta U(a_1\cdots a_{n-1})} \quad (33)$$

Notice that the first e-1 terms are identical so that (33) can be rewritten

$$C_n(L,\beta) = \ell^n(e-1)\sum_{a_1=0}^{F}\sum_{a_2=0}^{F-a_1}\cdots\sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j} e^{-\beta U(a_1\cdots a_{n-1})}$$
$$+ \ell^n\sum_{x_1=0}^{F}\sum_{a_1=0}^{F-x_1}\sum_{a_2=0}^{F-x_1-a_1}\cdots\sum_{a_{n-1}=0}^{F-x_1-\sum_{j=1}^{n-2}a_j} e^{-\beta U(a_1\cdots a_n)} \quad (33')$$

After we complete the interchanges in order of summation, (33') becomes

$$C_n(L,\beta) = \ell^n(e-1)\sum_{a_1=0}^{F}\sum_{a_2=0}^{F-a_1}\cdots\sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j} e^{-\beta U(a_1\cdots a_{n-1})}$$
$$+ \ell^n\sum_{a_1=0}^{F}\sum_{a_2=0}^{F-a_1}\cdots\sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j}\ \sum_{x_1=0}^{F-\sum_{j=1}^{n-1}a_j} e^{-\beta U(a_1\cdots a_{n-1})}$$

$$C_n(L,\beta) = \ell^n\sum_{a_1=0}^{F}\sum_{a_2=0}^{F-a_1}\cdots\sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j}\Big(F+e-\sum_{j=1}^{n-1}a_j\Big)e^{-\beta U(a_1\cdots a_{n-1})} \quad (33'')$$

Even this form is not the final form since we can make further simplification by taking advantage of the lattice symmetry. To do this we first define an additional variable

$$a_n = F - \sum_{j=1}^{n-1} a_j . \tag{34}$$

We showed earlier that the interaction energy is not changed when we translate all of the particles by an integral number of lattice constants. The quantity a_n defined above is also

$$\begin{aligned} a_n &= X_1 + N - X_n - e \\ \text{since } X_n &= X_1 + \sum_{j=1}^{n-1}(a_j + e) = X_1 + \sum_{j=1}^{n-1} a_j + (n-1)e \\ \Rightarrow X_1 + N - X_n - e &= X_1 + N - X_1 - \sum_{j=1}^{n-1} a_j - (n-1)e - e \\ &= N - ne - \sum_{j=1}^{n-1} a_j = F - \sum_{j=1}^{n-1} a_j \end{aligned} \tag{35}$$

a_n then is a quantity alike in character to the other a_j's in that it represents the number of free cells between two adjacent particles n and 1.

Let us compare the energy of two configurations, one represented by the set $(a_1, a_2, \cdots, a_{n-1})$, and a second $(a_2, a_3, \cdots, a_n)$. The second configuration can be developed from the first by translating the system until particle 1 is in cell N and relabelling particles to return them to numerical order. This is tantamount to a cyclic permutation of the ordered collection $(a_1, a_2, \cdots, a_n)$ and since it arises from a system translation we have the result.

$$U(a_1\, a_2 \cdots a_{n-1}) = U(a_2\, a_3 \cdots a_n)$$

We shall make use of this result in the discussion that follows.

With a bit of examination we can see that the sum in Equation (33") is a sum which is carried over those configurations for which $a_1 + a_2 + \cdots + a_n = F$ and only those. This means we can write Equation (33") in a more symmetric form by the use of a δ-function $\delta(F - \sum_{j=1}^{n} a_j)$ which is zero except when the argument vanishes in which case it is one.

$$C_n\,(L,\beta) = \ell^n \sum_{a_1=0}^{F} \sum_{a_2=0}^{F} \cdots \sum_{a_n=0}^{F} \delta(F - \sum_{j=1}^{n} a_j)\,(e + a_n)\, e^{-\beta U(a_1 \cdots a_{n-1})} \tag{36}$$

The order of summation as written now in Equation (36) does not matter since we have made the limits of each sum constant. Suppose that we now replace $u(a_1, a_2, \cdots, a_{n-1})$ by $u(a_2, a_3, a_4, \cdots, a_n)$. Since these two are equal, no change has occurred in (36). Now suppose we replace a_2 by a_1', a_3 by a_2', $\cdots$, a_n by a_{n-1}', a_1 by a_n'.

$$C_n(L,\beta) = \ell^n \sum_{a'_n=0}^{F} \sum_{a'_1=0}^{F} \cdots \sum_{a'_{n-1}=0}^{F} \delta\Big(F-\sum_{j=1}^{n-1} a'_j\Big)(e+a'_{n-1})\, e^{-\beta U(a'_1 a'_2 \cdots a'_{n-1})}$$

$$= \ell^n \sum_{a'_1=0}^{F} \cdots \sum_{a'_n=0}^{F} \delta\Big(F-\sum_{j=1}^{n} a'_j\Big)(e+a'_{n-1})\, e^{-\beta U(a'_1 \cdots a'_{n-1})} \qquad (37)$$

The a''s are only dummy variables so that we may now drop the primes noting that (37) looks just like (36) except that the factor $e + a_n$ is replaced by $e + a_{n-1}$. We can repeat this argument n times so that we have n different expressions all equal to $C_n(L,\beta)$. We write them all down and add

$$C_n(L,\beta) = \ell^n \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\Big(F-\sum_{j=1}^{n} a_j\Big)(e+a_n)\, e^{-\beta U(a_1 \cdots a_{n-1})}$$

$$= \ell^n \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\Big(F-\sum_{j=1}^{n} a_j\Big)(e+a_{n-1})\, e^{-\beta U(a_1 \cdots a_{n-1})}$$

$$= \ell^n \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\Big(F-\sum_{j=1}^{n} a_j\Big)(e+a_{n-2})\, e^{-\beta U(a_1 \cdots a_{n-1})}$$

$$\vdots$$

$$= \ell^n \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\Big(F-\sum_{j=1}^{n} a_j\Big)(e+a_1)\, e^{-\beta U(a_1 \cdots a_{n-1})}$$

$$\therefore\ n\,C_n(L,\beta) = \ell^n \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\Big(F-\sum_{j=1}^{n} a_j\Big)\Big(ne+\sum_{k=1}^{n} a_k\Big)\, e^{-\beta U(a_1 \cdots a_{n-1})}$$

The sum $\sum_{j=1}^{n} a_j = F = N - ne$ so that we have

$$\begin{aligned} C_n(L,\beta) &= \ell^n \frac{N}{n} \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\Big(F - \sum_{j=1}^{n} a_j\Big) e^{-\beta u(a_1 \cdots a_{n-1})} \\ &= \ell^n \frac{N}{n} \sum_{a_1=0}^{F} \sum_{a_2=0}^{F-a_1} \cdots \sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2} a_j} e^{-\beta u(a_1 \cdots a_{n-1})} \end{aligned} \qquad (38)$$

Now that we have an expression for the configuration integral we shall examine it to see how much our problem has been simplified. The terms of the original sum, Equation (23), were of the form $e^{-\beta u}$ while in (38) they have the form $\frac{N}{n} e^{-\beta u}$. Hence we have reduced the number of terms by N/n. There are $\binom{F + n - 1}{n - 1}$ terms in (38) so that there are $\frac{N}{n}\binom{F + n - 1}{n - 1}$ terms in (23). If $e = 1$, $F = N - n$, then in this case there are $\frac{N}{n}\binom{N - 1}{n - 1} = \binom{N}{n}$ terms. This means that if $e = 1$ the configuration integral for the case where the only interaction is the hard core repulsion is $C_n(L,\beta) = \ell^n \binom{N}{n}$ in agreement with the results obtained by Tross[5].

With the computation of $C_n(L,\beta)$, we now arrive at the next difficulty in the treatment of the lattice gas. In the case of continuum systems we find the pressure of a system by employing a derivative. Letting P represent the thermodynamic pressure we would find P by the following

$$P = \frac{1}{\beta} \frac{d}{dL} \ln Q_n(L,\beta) \qquad (39)$$

This, of course, cannot be applied in the case of the discrete lattice since L takes on only values which are integral multiples of the lattice constant ℓ. There are several alternative approaches to employ in computing P.

1. We can evaluate the derivative d/dL by noting $L = N\ell$. If we assume that the number of lattice points stays fixed we vary the volume by varying the lattice parameter. Hence $d/dL = 1/N \; d/d\ell$. When we write the potential interaction in its original form as Equation (5) we observe the dependence of u on ℓ. Let us look at the result for the system we just solved $C_n(L,\beta) = \ell^n \frac{N}{n}\binom{F + n - 1}{n - 1}$. This solution is the configuration integral for the Tonks gas[7] system with particles of size e. The partition function $Q_n(L,\beta) = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{n}{2}} \ell^n \frac{N}{n}\binom{F + n - 1}{n - 1}$ yields the following result for the pressure using our first method.

$$P = \frac{n}{N\beta} = \frac{n}{N} kT \tag{40}$$

Equation (40) is the equation of the pressure of an ideal gas but no account is taken of the volume occupied by particles and thus is not satisfactory. The other two methods work under the assumption that the lattice parameter is fixed and the number of lattice points varies. We make use of the calculus of finite differences and hence a short digression on this subject seems in order.

We first define the difference operator Δ on a function f(x) as

$$\Delta f(x) = f(x+1) - f(x) \tag{41}$$

Δ is sometimes called the forward difference operator. It has many of the properties of the differential operator in that it is distributive $\Delta(f + g) = \Delta f + \Delta g$ also $\Delta af = a\Delta f$ where a is constant. There is a slight difference in that $\Delta f(x)g(x) = f(x+1)\Delta g(x) + g(x)\Delta f(x)$.

We can also define an integration operation analogous to Riemann integration in real variables.

$$\sum\nolimits_a^b f(x) = \sum_{x=a}^{b-1} f(x) \tag{42}$$

With this definition we note

$$\sum\nolimits_a^b \Delta g(x) = \sum_{x=a}^{b-1} \Delta g(x) = g(b) - g(a) \tag{43}$$

Equation (43) is strongly reminiscent of the fundamental theorem of calculus[8]. We can set up difference formulas in a manner analogous to differential calculus.

$$\begin{aligned} \Delta a &= 0 \qquad \text{(a constant)} \\ \Delta ax &= a \end{aligned} \tag{44}$$

The combinatorial function $\binom{x}{n} = \frac{x!}{n!(x-n)!}$ behaves in difference calculus like $x^n/n!$ in differential calculus in that

$$\Delta \binom{x}{n} = \binom{x}{n-1} \tag{45}$$

With this bit of discussion of the difference calculus, we proceed to the second method for computing P. 2. We approximate the derivative d/dL by taking the difference of ln $Q_n(L,\beta)$ as L changes by ℓ or N changes by 1.

$$\begin{aligned} P &= \frac{1}{\beta\ell}\left(\ln Q_n(L+\ell,\beta) - \ln Q_n(L,\beta)\right) \\ &= \frac{1}{\beta\ell}\Delta \ln Q_n(N\ell,\beta) \end{aligned} \tag{46}$$

$Q_n(N\ell,\beta) = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{n}{2}} \ell^n C_n(N\ell,\beta)$. The only part of $Q_n(N\ell,\beta)$ that depends on L is the configuration integral $C_n(N\ell,\beta)$. Thus

$$P = \frac{1}{\beta\ell}\,\Delta \ln C_n(N\ell,\beta) \tag{47}$$

The third method is similar. We take as our expression for P

$$P = \frac{1}{\beta\ell}\,\frac{\Delta C_n(N\ell,\beta)}{C_n(N\ell,\beta)} \tag{48}$$

Equation (48) is the approximation to $P = \frac{1}{\beta C_n(L,\beta)} \frac{d}{dL} C_n(L,\beta)$ which is the result of Equation (39). We shall take the third form as being closest to the continuum form for the pressure in our system. The two forms Equations (47) and (48) merge together in the limit $\ell \to 0$.

We pick the third method because it seems closest to the form of $\frac{1}{C_n(L,\beta)} \frac{d}{dL} C_n(L,\beta)$ while $\Delta \ln C_n(N\ell,\beta) = \ln[1 + \frac{\Delta C_n(N,\ell,\beta)}{C_n(N\ell,\beta)}]$ which differs from Equation (48) except in the limit $\ell \to 0$. The first method is unsatisfactory because it does not take into account the additional configurations which arise from increased volume. If we use our method to compute the pressure for the Tonks gas we obtain

$$P = \frac{1}{\beta\ell} \frac{\Delta \frac{N}{n}\binom{F+n-1}{n-1}}{\frac{N}{n}\binom{F+n-1}{n-1}}$$

$$= \frac{1}{\beta\ell} \frac{1}{\frac{N}{n}\binom{F+n-1}{n-1}} \left[\frac{1}{n}\binom{F+n}{n-1} + \frac{N}{n}\binom{F+n-1}{n-2}\right] \tag{49}$$

$$= \frac{1}{\beta\ell}\left[\frac{1}{N}\,\frac{F+n}{F+1} + \frac{n-1}{F+1}\right] = \frac{1}{\beta\ell}\left[\frac{n-1+\frac{F+n}{N}}{F+1}\right]$$

When e = 1, (49) becomes $P = \frac{n}{\beta\ell(F+1)} \simeq \frac{n}{\beta\ell F}$. Now ℓF is just the free volume of the system, i.e., the empty volume.

$P \approx \frac{n}{\beta(L - n\ell)}$. In this form we have the usual Tonks gas result. This demonstrates the validity of the model; it can and does give reasonable and accurate results. As we shall see later when we examine the results of our numerical calculations, some of the pressure-volume curves are rather strange but this strangeness is not the result of the method of computation but rather is the result of the boundary conditions.

Let us now consider another problem, the one-dimensional Ising lattice gas generalized so that particle size is not cell size. The potential of the Ising model is defined by

$$V(x) = \begin{matrix} \infty & ; & x < e \\ -\epsilon & ; & e \leq x < e+1 \\ 0 & ; & x \geq e+1 \end{matrix} \tag{50}$$

The formulation we have gone through automatically builds in the hard core repulsion part of (50). Let us write down $u(a_1 \cdots a_{n-1})$ for the Ising lattice gas

$$u(a_1 \cdots a_{n-1}) = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \Big[V\Big(\sum_{k=i}^{j-1} a_k + (j-i)e\Big) + V\Big(N - \sum_{k=i}^{j-1} a_k - (j-i)e\Big) \Big] \tag{51}$$

The minimum value for $j - i$ in (51) is 1 the first term vanishes when $j - i > 1$, $a_i > 0$. The second term vanishes except when $N - \sum_{k=i}^{j-1} a_k - (j - i)e = e$. This can happen only if j=n and i=1 for then $N - \sum_{k=1}^{n-1} a_k - (n-1)e = e$ or $N - ne - \sum_{k=1}^{n-1} a_k = 0 \Longrightarrow a_n = 0$. Summarizing these results we see that the only contributions to u are from those terms containing a single a_j and then only when that a_j is zero.

$$U(a_1 \cdots a_n) = -\epsilon \sum_{k=1}^{n} \delta(a_k) \tag{51'}$$

We represent a configuration by the n-tuple $(a_1, a_2, \cdots, a_n)$ and from (51') we obtain the energy by counting the a_i's which vanish and multiplying the result by $-\varepsilon$. There are n different energy states in general if $F > 0$. These states are $-(n-1)\varepsilon, -(n-2)\varepsilon, \cdots, 0$. If $F = 0$ there is but one state $-n\varepsilon$ but this is a special case. The configuration integral then can be written as

$$C_n(L,\beta) = \ell^n \frac{N}{n} \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\Big(F - \sum_{j=1}^{n} a_j\Big) e^{\beta\epsilon \sum_{k=1}^{n} \delta(a_k)} \tag{52}$$

We evaluate (52) by finding the multiplicity of each level. The level $-(n-1)\varepsilon$ can occur in n ways, namely all $a_j = 0$ except one which is F. Since there are n choices of the a_j which can take on the value F, the multiplicity of the level $-(n-1)\varepsilon$ is n. The next level is $-(n-2)\varepsilon$. In order to achieve this energy, two of the a_j's must be nonzero and the rest zero. We now have a counting problem to determine the multiplicity of this level. Since two coordinates a_j must be nonzero, we assure this by taking 2 away from F and assigning a 1 to each of the two. This leaves F-2 to distribute between the two nonzero values. This problem is analogous to the problem of counting the number of ways of putting F-2 balls into 2 urns $\binom{F - 2 + 2 - 1}{F - 2} = \binom{F - 1}{F - 2}$. We can do this for each pair of coordinates a_i and a_j we choose from the collection of n. We can select the pairs in $\binom{n}{2}$ ways. The next level is $-(n - 3)\varepsilon$. This energy level occurs when 3 of the a_i's are nonzero. To assure that the three are nonzero, we assign each the starting value 1. This leaves F-3 to be distributed among the three. This can be done in in $\binom{F - 3 + 3 - 1}{F - 3} = \binom{F - 1}{F - 3}$ ways. There are $\binom{n}{3}$ ways of selecting 3 objects from a collection of n. The level $-(n - k)\varepsilon$ can occur in $\binom{n}{k}\binom{F - 1}{F - k}$ ways since as in the above discussion the level is only achieved when k of the a_i's are nonzero. We assure they are nonzero by assigning each the starting value 1 and distributing the remaining F-k among the k coordinates. There are $\binom{F - k + k - 1}{F - k} = \binom{F - 1}{F - k}$ ways of doing this. Since there are $\binom{n}{k}$ ways of selecting the k nonzero coordinates, there is a total degeneracy of this level of $\binom{n}{k}\binom{F - 1}{F - k} = \binom{n}{k}\binom{F - 1}{k - 1}$. We sum over all states to obtain $C_n(L,\beta)$.

$$C_n(L,\beta) = \ell^n \frac{N}{n} \sum_{k=1}^{n} \binom{n}{k} \binom{F-1}{k-1} e^{\beta\epsilon(n-k)} \tag{53}$$

Some of the terms in (53) may vanish because some levels may not be accessible to the system; e.g., if F = 1, only the level $-(n-1)\varepsilon$ is available; all other terms vanish. We note that if F = 1 when k > 1 the lower member of $\binom{F-1}{k-1}$ exceeds the upper member. This is equivalent to asking ourselves how many combinations of m things n at a time are there. If n exceeds m there are 0 such combinations. For the sake of consistency take $\binom{m}{n} = 0$ if $n > m$. With this definition, the sum (53) will fit all situations. The result (53) becomes identical to that found by Tross in his papers[5] with the aid of the computer.

(2) Grand Ensemble

Suppose we turn our attention now to the grand ensemble. We form the grand partition function as

$$\mathcal{Z}_V(Z,\beta) = \sum_{n=0}^{\infty} Z^n Q_n(V,\beta). \tag{54}$$

We can regard (54) as a transformation of variable from the discrete variable n to the continuous variable Z. We also regard this as a new ensemble and take as thermodynamic parameters the ensemble averages of the quantities from canonical calculations. We take as the number of particles in our system the ensemble average of the number n

$$\bar{n} = \frac{\sum_{n=0}^{\infty} n\, z^n Q_n(V,\beta)}{\sum_{n=0}^{\infty} z^n Q_n(V,\beta)} = z\frac{d}{dz} \ln \mathcal{Z}_V(z,\beta) . \tag{55}$$

Also recall that for a continuum system $\beta P = \frac{d}{dV} \ln Q_n(V,\beta) = \frac{\frac{\partial Q_n}{\partial V}(V,\beta)}{Q_n(V,\beta)}$. Therefore

$$\beta \bar{P} = \frac{1}{\mathcal{Z}_V(z,\beta)} \sum_{n=0}^{\infty} \beta P\, z^n Q_n(V,\beta) = \frac{d}{dV} \ln \mathcal{Z}_V(z,\beta) \tag{56}$$

This is not the usual form presented for pressure in the grand ensemble. We obtain the usual form by averaging the result (56) over all volumes from 0 to V.

$$\beta \bar{\bar{P}} = \frac{1}{V} \int_0^V dV \frac{d}{dV} \ln \mathcal{Z}_V(z,\beta) = \frac{1}{V} \ln \mathcal{Z}_V(z,\beta) \tag{57}$$

The form (57) is the one usually given for P in the grand ensemble and as Yang[9] has pointed out, the value $\bar{\bar{P}}$ in (57) can truly be identified with pressure only in the thermodynamic limit. Nevertheless, it is useful to observe the behavior of this function for finite systems in order to observe its characteristics for signs of its limiting behavior.

For the lattice system things are not so simple. Here the pressure P is taken as $\frac{1}{\beta}\frac{\Delta Q_n(N,\beta)}{Q_n(N,\beta)}$. Hence the ensemble average of P is

$$\bar{P} = \frac{1}{\beta}\,\frac{\sum_{n=0}^{\infty} z^{n}\,\Delta\,Q_{n}(N,\beta)}{\sum_{n=0}^{\infty} z^{n}\,Q_{n}(N,\beta)} = \frac{1}{\beta}\,\frac{\Delta\sum_{n=0}^{\infty} z^{n}\,Q_{n}(N,\beta)}{\sum_{n=0}^{\infty} z^{n}\,Q_{n}(N,\beta)} \qquad (58)$$

We can approximate the results of (58) as

$$\bar{P} \simeq \frac{1}{\beta}\,\Delta\,\ln \mathcal{Z}_{N}(z,\beta) \qquad (59)$$

We can now use (59) to evaluate the average of $\bar{P}$ over all values of N from 0 to N-1 so that

$$\begin{aligned}\bar{\bar{P}} &= \frac{1}{\beta N}\sum_{N'=0}^{N-1}\Delta\,\ln \mathcal{Z}_{N'}(z,\beta) = \frac{1}{\beta N}\sum_{0}^{N}\Delta\,\ln \mathcal{Z}_{N}(z,\beta)\\ &= \frac{1}{\beta N}\ln \mathcal{Z}_{N}(z,\beta)\end{aligned} \qquad (60)$$

Since the result (60) depends on the approximation (59) the grand ensemble results for pressure are exposed as being rather far removed from the canonical ensemble results. Using the result (60) to define the pressure in the grand ensemble, we can show that $\left(\frac{\partial P}{\partial \rho}\right)_{\beta} \geq 0$ where $\rho = \bar{n}/N$. We find $\frac{\partial P}{\partial \rho}$ as

$$\left(\frac{\partial P}{\partial \rho}\right)_{\beta} = \left(\frac{\partial P}{\partial z}\right)_{\beta} \Big/ \left(\frac{\partial \rho}{\partial z}\right)_{\beta} = N\left(\frac{\partial P}{\partial z}\right)_{\beta} \Big/ \left(\frac{\partial \bar{n}}{\partial z}\right)_{\beta} \qquad (61)$$

If $\beta PN = \ln \mathcal{Q}_N(Z,\beta)$, then

$$\beta N \left(\frac{\partial P}{\partial z}\right)_\beta = \frac{1}{\mathcal{Q}_N(z,\beta)} \sum_{n=0}^{\infty} n z^{n-1} Q_n(N,\beta) = \frac{\bar{n}}{z} \tag{62}$$

and

$$\left(\frac{\partial \bar{n}}{\partial z}\right)_\beta = \frac{\partial}{\partial z} \frac{\sum_{n=0}^{\infty} n z^n Q_n(N,\beta)}{\sum_{n=0}^{\infty} z^n Q_n(N,\beta)} = \frac{\overline{n^2} - \bar{n}^2}{z} \tag{63}$$

The quantity in (62) is obviously positive. To show that the result in (63) is positive, we need only recall that $\overline{n^2} - \bar{n}^2 = \overline{(n - \bar{n})^2}$ which is of necessity positive. $\Rightarrow \frac{\partial P}{\partial \rho} \geq 0$. We cannot guarantee such results for the canonical ensemble. Also, since $Q_0 = 1$ we have $\mathcal{Q}_N \geq 1 \Rightarrow \ln \mathcal{Q}_N \geq 0$, hence P is necessarily positive. Thus use of the grand ensemble formalism guarantees us that the pressure calculated will be positive and the P-ρ curve will be a monotonic curve with P increasing as ρ increases.

It is interesting to note that for the lattice system the point of departure is the canonical ensemble developed previously. Suppose we start with (21') as the equation for the configuration integral. We set $\ell = 1$ for convenience. This is not the simplest form of the configuration integral but we employ it for comparison with previous formulations. If e = 1 no more than N particles can occupy the N cells so that (54) becomes

$$\mathcal{Q}_N(z,\beta) = \sum_{n=0}^{N} z^n Q_n(N,\beta) \tag{54'}$$

We note that there is a relationship between $C_n(N,\beta)$ and $C_{N-n}(N,\beta)$. We establish its character by noting that for every configuration of particles present in the evaluation of $C_n(N,\beta)$ there is a corresponding one in the evaluation of $C_{N-n}(N,\beta)$. We establish this by noting that if we start with a configuration containing n particles and make the transformation $\sigma_j' = 1 - \sigma_j$ we arrive at a configuration which contains N-n particles and vice versa. The energies of the two configurations are related as follows.

$$U' = (N-2n)\sum_{j=1}^{N-1} V_j + U \tag{64}$$

From which we obtain

$$C_{N-n}(N,\beta) = e^{-\beta(N-2n)\sum_{j=1}^{N-1} V_j} C_n(N,\beta) \tag{65}$$

Using the result (65) together with Equation (3) in (54') yields

$$\mathcal{Q}_N(z,\beta) = \sum_{n=0}^{[N/2]} C_n(N,\beta)\left\{\left(z\sqrt{\frac{2\pi m}{\beta h^2}}\right)^n + \left(z\sqrt{\frac{2\pi m}{\beta h^2}}\right)^{N-n} e^{-\beta(N-2n)\sum_{j=1}^{N-1} V_j}\right\}. \tag{66}$$

If we let $z' = z\sqrt{\frac{2\pi m}{\beta h^2}}$ we obtain

$$\mathcal{Q}_N(z,\beta) = \sum_{n=0}^{[N/2]} C_n(N,\beta)\left\{z'^n + z'^{N-n} e^{-\beta(N-2n)\sum_{j=1}^{N-1} V_j}\right\} \tag{66'}$$

We have used the notation [N/2] to mean the largest integer that does not exceed N/2. Let $S = \sum_{j=1}^{N-1} V_j$ and $Z'' = Z'e^{-\beta S}$. With these substitutions we have

$$\begin{aligned} \mathcal{Z}_N(Z,\beta) &= \sum_{n=0}^{[N/2]} C_n(N,\beta)\left\{Z''^{\,n} e^{\beta n S} + Z''^{\,N-n} e^{\beta n S}\right\} \\ &= \sum_{n=0}^{[N/2]} C_n(N,\beta)\, e^{\beta n S}\left\{Z''^{\,n} + Z''^{\,N-n}\right\} \end{aligned} \tag{66''}$$

Now let $Z'' = e^{2\nu}$ then we have

$$\begin{aligned} \mathcal{Z}_N(Z,\beta) &= \sum_{n=0}^{[N/2]} C_n(N,\beta)\, e^{\beta n S}\left\{e^{2n\nu} + e^{2(N-n)\nu}\right\} \\ &= \sum_{n=0}^{[N/2]} C_n(N,\beta)\, e^{\beta n S} e^{N\nu}\left\{e^{-(N-2n)\nu} + e^{(N-2n)\nu}\right\} \\ &= \sum_{n=0}^{[N/2]} C_n(N,\beta)\, e^{N\nu+\beta n S}\left(2-\delta(n-\tfrac{N}{2})\right)\cosh(N-2n)\nu \end{aligned} \tag{67}$$

We insert the factor 2 to compensate for the 1/2 in the hyperbolic cosine. The δ-function corrects for double counting when n = N/2 in the case of even N. We write Equation (21')

$$C_n(N,\beta) = \frac{1}{n!}\sum_{x_1=1}^{N}\sum_{x_2=1}^{N}\cdots\sum_{x_n=1}^{N} e^{-\beta u(x_1\cdots x_n)} \tag{21'}$$

and realize that because of the hard core potential $u(x_1 \cdots x_n)$ is infinite when a pair of particles occupy the same site making the exponential go to zero for that situation. Thus the exponential in Equation (21') contributes only if all the x_i are distinct.

As it stands to here, the method is seen to correspond to the result Tross obtains after some torturous matrix arguments[5]. This demonstrates the simplicity and versatility of the point of view adopted for this work. Tross makes the further simplification that is made in this work of restricting the sum (21') to a single ordering of particles but fails to take advantage of the further reductions as we have. The reductions made herein reduce the number of terms that must be evaluated by a factor 1/N which is a significant saving and allows us to treat larger systems.

(3) The Pressure Ensemble

We have discussed the canonical ensemble and the grand canonical ensemble and found the usual results. There is another ensemble one can consider and even though it is not convenient for making computer calculations, it is most convenient for treating lattice systems theoretically. We transform the discrete variable F the free volume to the continuous variable ζ as follows

$$L(\zeta,\beta) = \sum_{F=0}^{\infty} \zeta^F C_n(ne+F,\beta) \; ; \quad \text{where } N = ne+F \tag{68}$$

Let us first establish the circle of convergence of the series. To do this we must determine the value of $\lim_{F\to\infty} \frac{C_n(ne+F+1,\beta)}{C_n(ne+F,\beta)} = \frac{1}{R}$ where R is the radius of convergence[10]. We can write

$$C_n(ne+F+1,\beta) = C_n(ne+F,\beta) + \Delta C_n(ne+F,\beta) \tag{69}$$

and so

$$\lim_{F\to\infty} \frac{C_n(ne+F+1,\beta)}{C_n(ne+F,\beta)} = 1 + \lim_{F\to\infty} \frac{\Delta C_n(ne+F,\beta)}{C_n(ne+F,\beta)} \tag{70}$$

The second quantity in the right hand member of (70) is just the limiting value of the pressure as the volume becomes very large. We seek the value of $\Delta C_n(ne + F,\beta)$.

An elementary application of difference calculus yields

$$\begin{aligned}\Delta C_n(ne+F,\beta) = {} & \frac{1}{N} C_n(ne+F,\beta) + \frac{N+1}{N} \sum_{a_1=0}^{F+1} \sum_{a_2=0}^{F+1-a_1} \cdots \sum_{a_{n-2}=0}^{F+1-\sum_{j=1}^{n-3} a_j} e^{-\beta U(a_1 \cdots a_{n-2},\, F+1-\sum_{k=1}^{n-2} a_k)} \\ & + \frac{N+1}{N} \sum_{a_1=0}^{F} \sum_{a_2=0}^{F-a_1} \cdots \sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2} a_j} \Delta e^{-\beta U(a_1 \cdots a_{n-1})}\end{aligned} \tag{71}$$

If we divide (71) by $C_n(ne + F,\beta)$ and take the limit we have

$$\begin{aligned}\lim_{F\to\infty} \frac{\Delta C_n(ne+F,\beta)}{C_n(ne+F,\beta)} & \\ = \lim_{F\to\infty} \frac{N+1}{N} & \frac{\sum_{a_1=0}^{F+1} \sum_{a_2=0}^{F+1-a_1} \cdots \sum_{a_{n-2}=0}^{F+1-\sum_{j=1}^{n-3} a_j} e^{-\beta U(a_1 \cdots a_{n-2},\, F+1-\sum_{k=1}^{n-2} a_k)}}{\frac{n}{N} C_n(ne+F,\beta)} \\ + \lim_{F\to\infty} \frac{N+1}{N} & \frac{\sum_{a_1=0}^{F} \sum_{a_2=0}^{F-a_1} \cdots \sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2} a_j} \Delta e^{-\beta U(a_1 \cdots a_{n-1})}}{\frac{n}{N} C_n(ne+F,\beta)}\end{aligned} \tag{72}$$

The interaction potential V(x) which we assume is such that for a finite number of particles u is bounded both from above and below. Thus, we can state

$$\frac{N+1}{N}\,\frac{\sum\limits_{a_1=0}^{F+1}\sum\limits_{a_2=0}^{F+1-a_1}\cdots\sum\limits_{a_{n-2}=0}^{F+1-\sum_{j=1}^{n-3}a_j} e^{-\beta u(a_1\cdots a_{n-2},\,F+1-\sum_{j=1}^{n-3}a_j)}}{\sum\limits_{a_1=0}^{F}\sum\limits_{a_2=0}^{F-a_1}\cdots\sum\limits_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j} e^{-\beta u(a_1\cdots a_{n-1})}}$$

$$\leq \frac{N+1}{N}\,\frac{(e^{-\beta u})_{max.}}{(e^{-\beta u})_{min.}}\,\frac{\binom{F+n-1}{n-2}}{\binom{F+n-1}{n-1}} \qquad (73)$$

The exponential function is positive for any real argument thus the term in (73) is bounded from below by zero. Since u is bounded both $(e^{-\beta u})_{max}$ and $(e^{-\beta u})_{min}$ are finite and nonzero.

$$\lim_{F\to\infty}\frac{\binom{F+n-1}{n-2}}{\binom{F+n-1}{n-1}} = \lim_{F\to\infty}\frac{n-1}{F+1} = 0 \qquad (74)$$

Now (73) and (74) together imply that

$$\lim_{F\to\infty}\frac{\Delta C_n(ne+F,\beta)}{C_n(ne+F,\beta)} = \lim_{F\to\infty}\frac{N+1}{N}\,\frac{\sum\limits_{a_1=0}^{F}\sum\limits_{a_2=0}^{F-a_1}\cdots\sum\limits_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j}\Delta e^{-\beta u(a_1\cdots a_{n-1})}}{\sum\limits_{a_1=0}^{F}\sum\limits_{a_1=0}^{F-a_1}\cdots\sum\limits_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2}a_j} e^{-\beta u(a_1\cdots a_{n-1})}} \qquad (75)$$

The right member of (75) must vanish if the periodic boundary conditions are to give useful results. The periodic nature of the potential causes the total interaction to depend on the number of lattice points. Thus we should assume that (75) vanishes and examine the results of this assumption. If P does not vanish with large volume, then it is this assumption which fails and in this event we should question the utility of the periodic boundary conditions. Thus we take

$$\lim_{F\to\infty} \frac{C_n(ne+F+1,\beta)}{C_n(ne+F,\beta)} = 1 + \lim_{F\to\infty} \frac{\Delta C_n(ne+F,\beta)}{C_n(ne+F,\beta)} = 1 \tag{76}$$

The result (76) therefore implies that the series in (68) converges for $|\zeta| < 1$. Suppose we now examine (68) more closely. We note that

$$C_n(ne+F,\beta) = \frac{1}{2\pi i} \oint \frac{L(\zeta,\beta)}{\zeta^{F+1}}\, d\zeta \tag{77}$$

Where the contour in (77) lies inside the unit circle and encloses the origin, now the function $\frac{L(\zeta,\beta)}{\zeta^{F+1}}$ is continuous and analytic for $\zeta \neq 0$. There is a pole of order F + 1 at the origin and since the radius of convergence is 1 $L(1,\beta) \to \infty$. Therefore somewhere along the real axis $\frac{L(\zeta,\beta)}{\zeta^{F+1}}$ has a minimum for $0 < \zeta < 1$. We can thus employ saddle-point integration to estimate $C_n(ne + F,\beta)$. We first rewrite the integral (77). Let us assume the countour C is a circle centered on the origin and having a radius $r < 1$. Let $\zeta = re^{i\theta}$ where $i = \sqrt{-1}$ the imaginary unit.

$$C_n(ne+F,\beta) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{L(re^{i\theta},\beta)}{r^F e^{iF\theta}}\, d\theta \tag{78}$$

Let $f(r,\theta) = \ln L(re^{i\theta},\beta)$ and $F(r,\theta) = f(r,\theta) - F \ln r - iF\theta$. From what has been said previously, we know that the integrand function $e^{F(r,\theta)}$ has a minimum along the real axis at some point, say $r = t$. We have then

$$\frac{\partial}{\partial r} e^{F(r,\theta)} \Big|_{\substack{r=t \\ \theta=0}} = 0 = F_r(r,\theta)\, e^{F_r(r,\theta)} \Big|_{\substack{r=t \\ \theta=0}} = \left(f_r(r,\theta) - \frac{F}{r} \right) e^{F(r,\theta)} \Big|_{\substack{r=t \\ \theta=0}} \tag{79}$$

The exponential does not vanish so that the parenthesis must go to zero. Consider

$$\frac{\partial}{\partial \theta} e^{F(r,\theta)} \Big|_{\substack{r=t \\ \theta=0}} = 0 = F_\theta(r,\theta)\, e^{F(r,\theta)} \Big|_{\substack{r=t \\ \theta=0}} \tag{80}$$

From the substitutions we have made, we note that $f_r = \frac{\partial}{\partial \zeta} \ln L \frac{\partial \zeta}{\partial r}$ and $f_\theta = \frac{\partial}{\partial \zeta} \ln L \frac{\partial \zeta}{\partial \theta}$; thus we have $\frac{f_\theta}{ire^{i\theta}} = \frac{f_r}{e^{i\varepsilon}}$ or

$$f_\theta = i r f_r \tag{81}$$

Using (81) in (80) shows that if (79) vanishes, (80) must also. To examine the nature of the point $r = t$, $\theta = 0$ we take the second derivatives.

$$\frac{\partial^2}{\partial r^2} e^{F(r,\theta)} \Big|_{\substack{r=t \\ \theta=0}} = \left(f_{rr}(r,\theta) + \frac{F}{r^2} \right) e^{F(r,\theta)} \Big|_{\substack{r=t \\ \theta=0}} > 0 \tag{82}$$

The result in (82) must be positive if $e^{F(r,\theta)}$ has a minimum at r for $\theta = 0$.

$$\frac{\partial^2}{\partial\theta^2} e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}} = f_{\theta\theta}\, e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}} \tag{83}$$

Now (81) tells us $f_\theta = irf_r$. From this we can show $f_{\theta\theta} = irf_{r\theta}$, $f_{\theta r} = if_r + irf_{rr}$. $f_{\theta r} = f_{r\theta}$ therefore $f_{\theta\theta} = -rf_r - r^2 f_{rr}$. Hence

$$\begin{aligned}\frac{\partial^2}{\partial\theta^2} e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}} &= -\left(r f_r + r^2 f_{rr}\right) e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}}\\ &= -r^2\left(f_{rr} + \frac{f_r}{r}\right) e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}}\end{aligned} \tag{84}$$

From (79) we have $F/r^2 = f_r/r$; hence

$$\frac{\partial^2}{\partial r^2} e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}} = \left(f_{rr} + \frac{f_r}{r}\right) e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}} > 0 \tag{82'}$$

Comparing (82') with (84) we have then

$$\frac{\partial^2}{\partial\theta^2} e^{F(r,\theta)}\Big|_{\substack{r=t\\ \theta=0}} < 0 \tag{85}$$

The results (82) and (85) imply that the point $r = t$, $\theta = 0$ is a saddle point. Thus if we fix r at t, then the function $e^{F(t,\theta)}$ has a maximum at $\theta = 0$. Let us expand the function $F(t,\theta)$ in a Taylor series around $\theta = 0$.

$$F(t,\theta) = \ln L(t,\beta) - F\ln t - \frac{\theta^2}{2}\left\{\overline{F^2} - \overline{F}^2\right\} + \cdots \tag{86}$$

For large systems, the coefficient of θ^2 is quite large since it is the difference between the ensemble average of the free volume squared and the square of the average free volume over the pressure ensemble. This should not be confused with the value F in the left hand member of (77). If we choose our circular contour to be of radius t we have

$$\begin{aligned} C_n(ne+F,\beta) &= \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{\ln L(t,\beta) - F\ln t - \frac{\theta^2}{2}\{\overline{F^2}-\bar{F}^2\}+\cdots}\, d\theta \\ &\simeq \frac{1}{2\pi} L(t,\beta)\, t^{-F}\int_{-\infty}^{\infty} e^{-\frac{\theta^2}{2}(\overline{F^2}-\bar{F}^2)}\, d\theta \\ &= \frac{1}{2\pi} L(t,\beta)\, t^{-F}\sqrt{\frac{2\pi}{\overline{F^2}-\bar{F}^2}} \end{aligned} \tag{87}$$

We can rewrite (87) as

$$t^F C_n(ne+F,\beta) = \sqrt{\frac{1}{2\pi(\overline{F^2}-\bar{F}^2)}}\; L(t,\beta) \tag{87'}$$

(87') shows that most of the properties of L(t,β) come from a single term in the sum and hence shows that the pressure ensemble can give good results; that the ensemble averages give results which agree with the canonical ensemble results. For the pressure ensemble we find the free volume as the ensemble average

$$\bar{F} = \frac{\sum_{F=0}^{\infty} F\,\zeta^F C_n(ne+F,\beta)}{\sum_{F=0}^{\infty} \zeta^F C_n(ne+F,\beta)} = \zeta\frac{\partial}{\partial\zeta}\ln L(\zeta,\beta) \tag{88}$$

$$\beta\bar{P} = \frac{\sum_{F=0}^{\infty} \zeta^F \beta P\, C_n(ne+F,\beta)}{\sum_{F=0}^{\infty} \zeta^F C_n(ne+F,\beta)} = \frac{\sum_{F=0}^{\infty} \zeta^F \Delta C_n(ne+F,\beta)}{\sum_{F=0}^{\infty} \zeta^F C_n(ne+F,\beta)} \tag{89}$$

We can rewrite (89) as

$$\beta\bar{P} = \frac{1}{\zeta L(\zeta,\beta)} \sum_0^\infty \zeta^{F+1} \Delta C_n(ne+F,\beta) \tag{89'}$$

Now $\zeta^{F+1}\Delta C_n(ne + F,\beta) = \Delta\zeta^F C_n(ne + F,\beta) - C_n(ne + F,\beta)\zeta^F(\zeta-1)$ thus

$$\beta\bar{P} = -\frac{C_n(ne,\beta)}{L(\zeta,\beta)\zeta} + \frac{1-\zeta}{\zeta} \tag{89''}$$

For large n the first term in the right member of (89") will be quite small so that

$$\beta\bar{P} = \frac{1-\zeta}{\zeta} \tag{90}$$

Using (88) and (90) we can obtain the equation of state with $\bar{F}$ given as a function of $\bar{P}$ and β.

Before we apply our results, let us look back at the definition of the pressure ensemble partition function

$$L(\zeta,\beta) = \sum_{F=0}^{\infty} \zeta^F C_n(ne+F,\beta) \tag{68}$$

Let us substitute the form Equation (38) in (68) with N replaced by $ne + \sum_{j=1}^{n} a_j$.

$$L(\zeta,\beta) = \sum_{F=0}^{\infty} \zeta^F \frac{1}{n} \sum_{a_1=0}^{F} \cdots \sum_{a_n=0}^{F} \delta\left(F - \sum_{j=1}^{n} a_j\right)\left(ne + \sum_{j=1}^{n} a_j\right) e^{-\beta u(a_1 \cdots a_n)} \tag{91}$$

If we carry out the sum over F we obtain

$$L(\zeta,\beta) = \frac{1}{n} \sum_{a_1=0}^{\infty} \cdots \sum_{a_n=0}^{\infty} \left(ne + \sum_{j=1}^{n} a_j\right) \zeta^{\sum_{j=1}^{n} a_j} e^{-\beta u(a_1 \cdots a_n)} \tag{92}$$

u becomes a function of the value a_n since u is dependent on the number of lattice points N which now is determined as $N = ne + \sum_{j=1}^{n} a_j$.

For convenience we define $F(\zeta,\beta)$

$$F(\zeta,\beta) = \sum_{a_1=0}^{\infty} \cdots \sum_{a_n=0}^{\infty} \prod_{j=1}^{n} \zeta^{a_j} e^{-\beta u(a_1 \cdots a_n)} \tag{93}$$

We have employed the notation $\prod_{i=1}^{n} f_i$ which is defined by $\prod_{i=1}^{n} f_i = f_1 \cdot f_2 \cdot f_3 \cdots f_n$. With the definition (93) we note that

$$L(\zeta,\beta) = \frac{1}{n}\left(ne + \zeta \frac{d}{d\zeta}\right) F(\zeta,\beta) \tag{94}$$

Let us now apply this ensemble to some examples. First the Tonks gas or the case u = 0. Here we obtain

$$F(\zeta,\beta) = \left(\frac{1}{1-\zeta}\right)^n \tag{95}$$

Employing (94) we obtain

$$L(\zeta,\beta) = \frac{1}{n}\left(\frac{ne}{(1-\zeta)^n} + \frac{\zeta}{(1-\zeta)^{n+1}}\right) = \frac{1}{n(1-\zeta)^{n+1}}\left(ne(1-\zeta)+\zeta\right) \tag{96}$$

Following the prescription outlined previously, we first find $\bar{F}$.

$$\bar{F} = \zeta\frac{d}{d\zeta}\ln L(\zeta,\beta) = (n+1)\frac{\zeta}{1-\zeta} + \frac{1-ne}{\zeta+ne(1-\zeta)} \tag{97}$$

When the number of particles n is large the second term of (97) is insignificant compared to the first so that

$$\bar{F} = \frac{(n+1)\zeta}{1-\zeta} = \frac{n+1}{\beta P} \qquad \text{see Eq. 90} \tag{97'}$$

For large n the 1 is insignificant so that we have

$$\beta\bar{P} = \frac{n}{\bar{F}} \tag{97"}$$

This form agrees with that which we obtained earlier for the pressure from the canonical ensemble.

The Ising model is also soluble in this ensemble. To obtain this solution we note that the interaction has been written

$$U(a_1\cdots a_n) = -\epsilon\sum_{j=1}^{n}\delta(a_j) \tag{51'}$$

If we use (51') in (93) we obtain

$$F(\zeta,\beta) = \left(\sum_{a_1=0}^{\infty} \zeta^{a_1} e^{\beta \epsilon \delta(a_1)}\right)^n \tag{98}$$

$$= \left(e^{\beta\epsilon} + \frac{\zeta}{1-\zeta}\right)^n$$

$$L(\zeta,\beta) = \frac{1}{n}\left\{ne'\left(e^{\beta\epsilon}+\frac{\zeta}{1-\zeta}\right)^n + \frac{n}{(1-\zeta)^2}\left(e^{\beta\epsilon}+\frac{\zeta}{1-\zeta}\right)^{n-1}\right\} \tag{99}$$

$$= \left(e^{\beta\epsilon}+\frac{\zeta}{1-\zeta}\right)^{n-1}\left[e'\left(e^{\beta\epsilon}+\frac{\zeta}{1-\zeta}\right) + \frac{1}{(1-\zeta)^2}\right].$$

For large n the term inside the square brackets is small compared to the other term and hence will contribute little to the resultant thermodynamic quantities. The quantity e' there is the particle diameter e. The prime is used to avoid confusion with the exponential e = 2.71828 ···.

$$\ln L(\zeta,\beta) \simeq (n-1)\ln\left(e^{\beta\epsilon}+\frac{\zeta}{1-\zeta}\right) \tag{100}$$

From which $\bar{F} = \dfrac{(n-1)\dfrac{1}{(1-\zeta)^2}}{e^{\beta\epsilon}+\dfrac{\zeta}{1-\zeta}} = \dfrac{n-1}{\zeta(1-\zeta)+(1-\zeta)^2 e^{\beta\epsilon}}$.

Using (90) we have

$$\bar{F} = \frac{n-1}{\dfrac{\beta P}{(1+\beta P)^2} + \left(\dfrac{\beta P}{1+\beta P}\right)^2 e^{\beta\epsilon}} = \frac{(n-1)(1+\beta P)^2}{\beta P + \beta^2 P^2 e^{\beta\epsilon}} \tag{101}$$

Equation (101) expresses the equation of state of the Ising lattice gas in the nearest neighbor interaction. This demonstrates the use of the pressure ensemble showing it to be of use in obtaining results where the other ensembles fail or are difficult to handle. The special form of the pressure ensemble makes it ideal to treat nearest neighbor interactions. Such works have been done for continuum systems and such results reveal that no transitional phenomena occur[11].

The pressure ensemble as considered here is well-suited to the theoretical investigations of lattice systems. Siegert and Lewis[12] discuss the pressure ensemble in the continuum and this discussion can be carried over to lattice systems with little difficulty. The pressure ensemble defined here is quite similar to the grand ensemble and thus the zeros of this function are of importance in the study of transitional phenomena.

CHAPTER III

DISCUSSION OF COMPUTER CALCULATIONS

A. Canonical Ensemble

We have previously discussed the derivation of the configuration integral $C_n(L,\beta)$. We obtained the following result

$$C_n(L,\beta) = \ell^n \frac{N}{n} \sum_{a_1=0}^{F} \sum_{a_2=0}^{F-a_1} \cdots \sum_{a_{n-1}=0}^{F-\sum_{j=1}^{n-2} a_j} e^{-\beta U(a_1 \cdots a_{n-1})} \tag{38}$$

We shall assume that the lattice constant $\ell = 1$ and that we measure energy in units such that $k = 1$ (Boltzmann's constant). If $\ell = 1$, $L = N$ and so $C_n(L,\beta) = C_n(N,\beta)$. The sum (38) does not really take full advantage of all possible symmetry. We do not eliminate the duplications of configurations of the form $(a_1, a_2, \cdots, a_n)$. In fact, each cyclic permutation of this appears. We have a scheme then to reduce still further the sum (38). Let A be the row vector $(a_1, a_2, \cdots, a_n)$ which represents the configuration. We form all cyclic permutations of A and keep those in which the nth component is the largest component. There are n cyclic permutations of the row vector A; but, keeping only those in which the nth component is largest reduces this to k terms of this sort. k counts the number of components of

A equal to the largest component. The sum in (38) runs over all configurations like A in which the sum of the components is F. We impose the additional restriction on the sum that we sum only those configurations in which a_n is the largest component and we weight these terms by n/k. The value k depends on the configuration A. As we stated, k is the number of components of A equal to a_n. Thus k = $\sum_{j=1}^{n} \delta(a_n - a_j)$. On the computer we evaluate k by taking advantage of the manner in which the machine does its arithmetic. By our construction $a_n \geq a_k \forall k$. The machine performs fixed point division by dropping all digits to the right of the decimal point so that if $a_k < a_n$, $a_k/a_n = 0$ in fixed point arithmetic while if $a_k = a_n$; $a_k/a_n = 1$.

$\therefore k = \sum_{j=1}^{n} a_j/a_n$ evaluated in fixed point arithmetic

$$k = 1 + \sum_{j=1}^{n-1} a_j/a_n \tag{101}$$

We can indicate the evaluation of the configuration integral now as

$$C_n(N,\beta) = N \sum_{a_n=0}^{F} \sum_{a_1=0}^{a_n} \sum_{a_2=0}^{a_n} \cdots \sum_{a_{n-1}=0}^{a_n} \delta\left(F - \sum_{j=1}^{n} a_j\right) \frac{e^{-\beta U(a_1 \cdots a_{n-1})}}{1 + \sum_{j=1}^{n-1} a_j/a_n} \tag{102}$$

The purpose of our calculation is to obtain values for the thermodynamic quantities pressure, internal energy, heat capacity and the statistical correlation function. The pressure has already been discussed. We use $P = \frac{1}{\beta}\frac{\Delta C_n(N,\beta)}{C_n(N,\beta)}$ as our value for the pressure. The internal energy is found by applying the usual prescription which is just the average value of the Hamiltonian over the ensemble.

$$E = \langle H \rangle = -\frac{\partial}{\partial\beta}\ln Q_n(N,\beta) = \frac{n}{2\beta} + \langle u \rangle \tag{103}$$

$$\langle u \rangle = \frac{\sum u e^{-\beta u}}{\sum e^{-\beta u}} \tag{104}$$

The heat capacity is by definition $\left(\frac{\partial E}{\partial T}\right)_N$ so we evaluate this derivative to evaluate C_V the heat capacity. Using (103) and (104) we obtain

$$C_v = \frac{n}{2} + \beta^2\left[\langle u^2 \rangle - \langle u \rangle^2\right] \tag{105}$$

The second term in (105) is the fluctuation of the average internal energy multiplied by $\frac{1}{T^2}$. We can easily show that $\langle (u - \langle u \rangle)^2 \rangle = \langle u^2 \rangle - \langle u \rangle^2$ and since the first expression is positive definite $C_V \geq \frac{n}{2}$. As the temperature of a system increases, one expects the thermal vibration to increase and hence one expects the fluctuations to increase. In rough terminology, this means that as the temperature increases order decreases.

One aspect of the lattice system not emphasized previously is that the energy states available form a discrete set finite in size. Since the number of levels is finite the spacing between levels is also finite and hence there is a gap between the lowermost level and the next level. Normally we would expect a system to reside in its lowest energy state and we would find that here if thermal energy were not giving enough of a kick so that other levels can be populated. For convenience, we enumerate the energy levels as $u_1 < u_2 < \cdots < u_m$ where there are m distinct energy states. In the Tonks gas case, there was but one level. In the Ising lattice gas there were n levels. The ratio of probabilities of the lowest state over the next is

$$\frac{e^{-\beta u_1}}{e^{-\beta u_2}} = e^{-\beta(u_1 - u_2)} \tag{106}$$

$u_1 \leq u_2 \Rightarrow u_1 - u_2 \leq 0 \Rightarrow e^{-\beta(u_1 - u_2)} \to \infty$ as $\beta \to \infty$. This result means that at low enough temperature (large β since $\beta = 1/T$) the entire partition function is essentially given by $e^{-\beta u_1}$ multiplied by the multiplicity of this level. It is as if there were but one level u_1. The potential $V(x)$ has a minimum value for some value for x. At this separation the interaction between a pair of particles is a minimum. Thus to minimize the energy we maximize the number of times this separation occurs. This will tend to make the lowest state an ordered one, i.e., one with high correlation, at least for certain separations.

We can study the tendency toward ordering at low temperatures by studying the correlation function and its behavior as a function of temperature as well as separation. The correlation function for this calculation is determined most easily by the following considerations. We return to our original representation in terms of cell occupancy. The pair correlation function as defined in Hill[13] is given by

$$\mathrm{cor}(i,j) = \frac{W(i,j)}{W(i)\,W(j)} \tag{107}$$

Where W(i,j) is the probability that cells i and j are simultaneously occupied and W(i) is the probability cell i is occupied. We find the probability W(i) by summing over only those configurations in which cell i is occupied and divide this by the total configuration integral. We accomplish this by summing $\sigma_i e^{-\beta u}$ over all configurations. Since σ_i vanishes when cell i is empty, we effectively sum only over those configurations in which cell i is occupied. Thus

$$W(i) = \langle\sigma_i\rangle = \frac{\sum \sigma_i e^{-\beta u}}{\sum e^{-\beta u}} \tag{108}$$

From the symmetry of the lattice, it is clear that each cell has the same environment as any other $\Rightarrow \langle\sigma_i\rangle = \langle\sigma_j\rangle$. We know that there are n particles in the system so that

$$\sum_{j=1}^{N} \sigma_j = n \tag{109}$$

$$\Rightarrow \quad \left\langle \sum_{j=1}^{N} \sigma_j \right\rangle = n \tag{110}$$

$$\Rightarrow \quad \sum_{j=1}^{N} \langle \sigma_j \rangle = n \tag{111}$$

Since each of the expectation values in (111) is the same as any other

$$N \langle \sigma_i \rangle = n \quad \Rightarrow \quad \langle \sigma_i \rangle = \frac{n}{N} = \rho \; (\text{particle density}) \tag{112}$$

Putting this result in (108) we have

$$W(i) = \rho \tag{113}$$

The evaluation of W(i,j) proceeds along similar lines.

$$W(i,j) = \langle \sigma_i \sigma_j \rangle \tag{114}$$

As stated before, the environment of one cell is exactly like any other and nothing is changed if we relabel the cells calling cell i 1, cell i+1 2, etc. From this we can say

$$W(i,j) = \langle \sigma_1 \; \sigma_{1+j-i} \rangle \tag{115}$$

(115) tells us that the probability W(i,j) depends only on the difference of the values j and i. We could just as easily have relabelled cell i as 2 or 3 or 4 or ··· or N. Thus

$$W(i,j) = \langle \sigma_1 \, \sigma_{1+j-i} \rangle = \langle \sigma_2 \, \sigma_{2+j-i} \rangle = \cdots = \langle \sigma_N \, \sigma_{N+j-i} \rangle \tag{116}$$

If we add all of the terms in (116) we obtain

$$N\,W(i,j) = \sum_{k=1}^{N} \langle \sigma_k \, \sigma_{k+j-i} \rangle = \langle \sum_{k=1}^{N} \sigma_k \, \sigma_{k+j-i} \rangle \tag{117}$$

From (117) we can solve for W(i,j).

$$W(i,j) = \frac{1}{N} \langle \sum_{k=1}^{N} \sigma_k \, \sigma_{k+j-i} \rangle \tag{118}$$

If we refer back to Equation (6), we note that the term in angle brackets above is just the j-i$^{\text{th}}$ component of the profile.

$$W(i,j) = \frac{1}{N} \langle P_{j-i} \rangle \tag{119}$$

Let us look back at Equation (107) now to rewrite the correlation function

$$\operatorname{cor}(i,j) = \frac{1}{N\rho^2} \langle P_{j-i} \rangle \tag{120}$$

Since the correlation function depends only on the difference j-i we write the correlation function as a function of the difference so that

$$\operatorname{cor}(k) = \frac{1}{N\rho^2} \langle P_k \rangle = -\frac{1}{\beta N \rho^2} \frac{\partial}{\partial V_k} \ln C_n(N,\beta;\ V_1,\cdots,V_{N-1}) \tag{121}$$

Summary

We must compute several items by computer. We first compute the configuration integral

$$C_n(L,\beta) = N \sum_{a_n=0}^{F} \sum_{a_1=0}^{a_n} \cdots \sum_{a_{n-1}=0}^{a_n} \delta\left(F - \sum_{j=1}^{n} a_j\right) \frac{e^{-\beta u(a_1 \cdots a_{n-1})}}{1 + \sum_{k=1}^{n-1} a_k/a_n} \tag{122}$$

Along with this we must compute <u>, <u^2>, and <P_k> for k = 1, 2, ⋯ , N-1. Actually, we know that $P_k = P_{N-k}$ so that we need only compute averages for half of these values k = 1, 2, 3, ⋯ , [N/2].

We compute the pressure by

$$P = T \frac{\Delta C_n(N,\beta)}{C_n(N,\beta)} = T \frac{C_n(N+1,\beta) - C_n(N,\beta)}{C_n(N,\beta)}$$

the internal energy by

$$E = \frac{nT}{2} + \langle u \rangle$$

the heat capacity by

$$C_v = \frac{n}{2} + \frac{1}{T^2}\left[\langle u^2\rangle - \langle u\rangle^2\right]$$

and the correlation function by

$$\mathrm{cor}(k) = \frac{N}{n^2}\langle P_k\rangle$$

The actual computer program which evaluates these quantites is presented in the appendix. In the next section we discuss the calculation of thermodynamic properties in the grand ensemble.

B. Grand Canonical Ensemble

The partition function for the grand canonical ensemble has been defined as follows

$$\mathcal{Z}_N(z,\beta) = \sum_{n=0}^{\infty} z^n Q_n(N,\beta) \tag{123}$$

Where $Z = e^{\beta\mu}$; μ is the chemical potential. However, for our purposes Z is a just a parametric quantity. Any standard text in statistical mechanics will verify that the thermodynamic properties of a system are obtained from the grand ensemble as

$$\beta PN = \ln \mathcal{Z}_N(z,\beta) \tag{124}$$

$$\bar{n} = \frac{1}{\mathcal{Z}_N(z,\beta)} \sum_{n=0}^{\infty} n z^n Q_n(N,\beta) \tag{125}$$

Here P is the pressure $\bar{n}$ the average of the number of particles over the ensemble. We shall use a bar over a symbol to denote its average over the grand ensemble to distinguish this average from the canonical ensemble average denoted by angle brackets <>. The upper limit in (124) and (125) is infinite; however, for our system where we are using hard core repulsive potentials with hard core diameter e the quantities Q_n vanish for $n > N/e$ since these conditions cannot exist $\therefore$ we rewrite (123) as

$$\mathcal{Z}_N(z,\beta) = \sum_{n=0}^{N/e} z^n Q_n(N,\beta) \tag{123'}$$

For those cases where N/e is not an integer, the sum runs to the largest value which does not exceed N/e. This value is commonly symbolized as [N/e]. Thus, if N = 13 and e = 2, N/e = 6.5 but [N/e] = 6. We cannot force more than 6 particles into this system since each one occupies two cells. For e = 1, there are some special results. Equation (16) expresses the connection between the energies of an n particle configuration u to that of the corresponding N-n particle configurations u' both in N cells. If we make the transformation as in (15)

$$\sigma_j' = 1 - \sigma_j \tag{15}$$

We exchange occupied cells for unoccupied ones and unoccupied cells for occupied ones. Thus as we show in (16)

$$u' = (N-2n)\sum_{j=1}^{N-1} V_j + u . \tag{16}$$

The transformation (15) is a 1-1 and onto mapping thus it possesses an inverse which is obviously $\sigma_j = 1 - \sigma_j'$. This shows that there is a 1-1 and onto connection between the configurations in $C_n(N,\beta)$ and $C_{N-n}(N,\beta)$. Now we have

$$C_{N-n}(N,\beta) = \sum_{\{\text{configurations}\}} e^{-\beta u'} = \sum_{\{\text{config.}\}} e^{-\beta(N-2n)\sum_{j=1}^{N-1} V_j - \beta u} \tag{126}$$

$$\Rightarrow C_{N-n}(N,\beta) = e^{-\beta(N-2n)\sum_{j=1}^{N-1} V_j} C_n(N,\beta) \tag{127}$$

For the case e = 1, we can write the sum (123') as

$$\mathcal{Q}_N(Z,\beta) = \sum_{n=0}^{N} Z^n Q_n(N,\beta) \tag{123'}$$

We showed previously that $Q_n(N,\beta) = (\frac{2\pi m}{\beta h^2})^{n/2} C_n(N,\beta)$

$$\mathcal{Q}_N(Z,\beta) = \sum_{n=0}^{N} \left(Z\sqrt{\frac{2\pi m}{\beta h^2}}\right)^n C_n(N,\beta) \tag{123''}$$

If we replace $Z\sqrt{\frac{2\pi m}{\beta h^2}}$ by Z' we have

$$\mathcal{Q}_N(Z,\beta) = \sum_{n=0}^{N} Z'^n C_n(N,\beta) \tag{128}$$

Using the result we have just obtained, we can rewrite (128)

$$\begin{aligned}\mathcal{Q}_N(Z,\beta) &= \sum_{n=0}^{[N/2]} \left(Z'^n C_n(N,\beta) + Z'^{N-n} C_n(N,\beta) e^{-\beta(N-2n)\sum_{j=1}^{N-1} V_j} \right) \\ &= \sum_{n=0}^{[N/2]} C_n(N,\beta)\, e^{\beta n \sum_{j=1}^{N-1} V_j} \Big(\big(Z' e^{-\beta\sum_{j=1}^{N-1} V_j}\big)^n \\ &\qquad + \big(Z' e^{-\beta \sum_{j=1}^{N-1} V_j}\big)^{N-n} \Big)\end{aligned} \tag{128'}$$

Finally replacing $Z' e^{-\beta \sum_{j=1}^{N-1} V_j}$ by Z" we have

$$\mathcal{Q}_N(Z,\beta) = \sum_{n=0}^{[N/2]} C_n(N,\beta)\, e^{n\beta\sum_{j=1}^{N-1} V_j} \left(Z''^n + Z''^{N-n} \right) \tag{128''}$$

$$Z'' = Z\sqrt{\frac{2\pi m}{\beta h^2}}\; e^{-\beta \sum_{j=1}^{N-1} V_j} \tag{129}$$

It is important to note that Z" depends not only on Z but also on β and the components of the potential V_j. So long as we do not vary the temperature or potential, we can regard Z" just as we regard Z, namely as a convenient parameter to give us a set of parametric equations for P and $\bar{n}$. For convenience, let P = $\bar{n}/N$ and call it the particle density or just the density by analogy with Equation (112). Thus we evaluate the partition function $\mathcal{Q}_N(Z,\beta)$ as follows

$$\mathcal{Q}_N(Z,\beta) = \sum_{n=0}^{[\frac{N}{2}]} C_n(N,\beta)\, e^{n\beta\sum_{j=1}^{N-1} V_j} \left(Z''^{\,n} + Z''^{\,N-n} \right) \tag{128"}$$

$$\rho = \bar{n}/N = \frac{1}{N\,\mathcal{Q}_N(Z,\beta)} \sum_{n=0}^{[N/2]} C_n(N,\beta)\, e^{n\beta\sum_{j=1}^{N-1} V_j} \left(n Z''^{\,n} + (N-n) Z''^{\,N-n} \right) \tag{130}$$

In addition to the pressure and density, we wish to evaluate the internal energy and heat capacity as well as the correlation function. The internal energy in the grand ensemble system is found in a manner like the internal energy in the canonical ensemble.

$$\bar{E} = \frac{\bar{n}T}{2} + \overline{\langle u \rangle} = \overline{\langle H \rangle} \tag{131}$$

As before, the bar above a quantity indicates average over the grand ensemble. The second term in the right member in (131) is a double average over both ensembles. We use the form Equation (131) to compute the internal energy.

We also wish to find the heat capacity in the grand ensemble. This is not as simple as the corresponding evaluation of the canonical ensemble. The heat capacity is found as the temperature derivative of the internal energy $\bar{E}$ computed in (131). However, we cannot compare the canonical ensemble and grand ensemble heat capacities because $\bar{n}$ also depends on temperature. The quantity $\bar{E}$ depends on the parameter Z, the number of cells N, and the temperature $T = 1/k\beta$. The difference in the two ensembles as far as heat capacity is concerned is that in the canonical ensemble the number of particles n is fixed and thus does not vary with temperature. To evaluate the heat cap., we take the temperature derivative while holding $\bar{n}$ fixed. This will put it more in line with the canonical calculation. Fixing the value $\bar{n}$ imposes an implicit relationship between Z and β. $\bar{n}$ depends on Z, β, and N but N is fixed in both ensembles so that we regard it as a constant and suppress it although it is still implicitly present. Now $\bar{E} = \bar{E}(Z,\beta)$ and $\bar{n} = \bar{n}(Z,\beta)$. We must now make use of the chain rule for differentiation to find C_V as the derivative of $\bar{E}$ with respect to temperature while the average number of particles $\bar{n}$ is held fixed. In symbols, this is

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_{\bar{n}} \tag{132}$$

As stated, $\bar{E}$ is explicitly a function of Z and β as is $\bar{n}$. Holding $\bar{n}$ fixed forces a relationship between Z and β. Thus $\bar{E}(Z,\beta) = \bar{E}(\beta,\bar{n})$. β is defined as 1/kT so that

$$\frac{\partial}{\partial T} = -\beta^2 \frac{\partial}{\partial \beta} \quad (\text{we assume } k = 1.) \tag{133}$$

Thus $C_v = -\beta^2 \left(\frac{\partial}{\partial \beta} \bar{E}\right)_{\bar{n}}$

$$\left(\frac{\partial \bar{E}}{\partial \beta}\right)_{\bar{n}} = \left(\frac{\partial \bar{E}}{\partial \beta}\right)_z + \left(\frac{\partial \bar{E}}{\partial z}\right)_\beta \left(\frac{\partial z}{\partial \beta}\right)_{\bar{n}} \tag{134}$$

We wish to evaluate $(\frac{\partial z}{\partial \beta})_{\bar{n}}$. This we can do as follows

$$d\bar{n} = \left(\frac{\partial \bar{n}}{\partial z}\right)_\beta dz + \left(\frac{\partial \bar{n}}{\partial \beta}\right)_z d\beta = 0$$

$$\Longrightarrow \left(\frac{\partial z}{\partial \beta}\right)_{\bar{n}} = -\left(\frac{\partial \bar{n}}{\partial \beta}\right)_z \Big/ \left(\frac{\partial \bar{n}}{\partial z}\right)_\beta \tag{135}$$

Thus we have

$$C_v = -\beta^2 \left\{ \left(\frac{\partial \bar{E}}{\partial \beta}\right)_z - \left(\frac{\partial \bar{E}}{\partial z}\right)_\beta \left(\frac{\partial \bar{n}}{\partial \beta}\right)_z \Big/ \left(\frac{\partial \bar{n}}{\partial z}\right)_\beta \right\} \tag{136}$$

Now Equation (131) can be written out more fully as

$$\bar{E} = \frac{\sum_{n=0}^{N} \langle H \rangle \, z^n Q_n(N,\beta)}{\mathcal{Q}_N(z,\beta)} \tag{137}$$

It is shown in the standard works on statistical mechanics that

$$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Q_n(N,\beta) = -\frac{1}{Q_n(N,\beta)} \frac{\partial}{\partial \beta} Q_n(N,\beta) \tag{138}$$

Thus we can evaluate $(\frac{\partial \bar{E}}{\partial \beta})_Z$ quite easily obtaining

$$\left(\frac{\partial \bar{E}}{\partial \beta}\right)_z = -\left[\overline{\langle H^2 \rangle} - \overline{\langle H \rangle}^2\right] \tag{139}$$

We also need to evaluate $(\frac{\partial \bar{E}}{\partial Z})_\beta$. By noting that

$$\bar{n} = z \frac{d}{dz} \ln \mathcal{Z}_N(z,\beta) \tag{140}$$

we can evaluate $(\frac{\partial \bar{E}}{\partial Z})_\beta$ easily obtaining

$$\left(\frac{\partial \bar{E}}{\partial z}\right)_\beta = \frac{1}{z}\left[\overline{n\langle H \rangle} - \bar{n}\,\overline{\langle H \rangle}\right] \tag{141}$$

Finally, we need $(\frac{\partial \bar{n}}{\partial Z})_\beta$ and $(\frac{\partial \bar{n}}{\partial \beta})_Z$. For these we find

$$\left(\frac{\partial \bar{n}}{\partial \beta}\right)_z = -\left[\overline{n\langle H \rangle} - \bar{n}\,\langle H \rangle\right] \tag{142}$$

and

$$\left(\frac{\partial \bar{n}}{\partial z}\right)_\beta = \frac{1}{z}\left[\overline{n^2} - \bar{n}^2\right] \tag{143}$$

Combining (136), (139), (141), (142), and (143), we obtain

$$C_v = \beta^2\left[\overline{\langle H^2 \rangle} - \overline{\langle H \rangle}^2 - \frac{\left(\overline{n\langle H \rangle} - \bar{n}\,\overline{\langle H \rangle}\right)^2}{\overline{n^2} - \bar{n}^2}\right] \tag{144}$$

Thus we need to compute $\overline{<H>}$, $\overline{<H^2>}$, $\bar{n}$, $\overline{n2}$, and $\overline{n<H>}$ to compute C_V.

Finally, we wish to compute the correlation function cor(k). This is done in a manner entirely analogous to the canonical computation.

$$\mathrm{cor}(k) = \frac{N}{\bar{n}^2} \overline{\langle P_k \rangle} = -\frac{N}{\beta \bar{n}^2} \frac{\partial}{\partial V_k} \ln \mathcal{Q}_N(z,\beta; V_1 \cdots V_{N-1}) \quad (145)$$

This completes the computer set-up for the grand ensemble.

Summary

We use the same program we used in the canonical calculations to compute $C_n(N,\beta)$, $\langle u \rangle$, $\langle u^2 \rangle$. Then we employ these values in grand ensemble calculations. For e = 1 we compute the grand ensemble partition function as

$$\mathcal{Q}_N(z,\beta) = \sum_{n=0}^{[N/2]} C_n(N,\beta) e^{n\beta \sum_{j=1}^{N-1} V_j} \left(z''^{\,n} + z''^{\,N-n} \right) \quad (128'')$$

and the density as

$$\rho = \frac{\bar{n}}{N} = \frac{1}{\mathcal{Q}_N(z,\beta)} \sum_{n=0}^{[N/2]} C_n(N,\beta) e^{n\beta \sum_{j=1}^{N-1} V_j} \left(n z''^{\,n} + (N-n) z''^{\,N-n} \right) \quad (130')$$

For e > 1 we revert to the original form (123') for use in computing the partition function and all the averages.

CHAPTER IV

PRESENTATION OF COMPUTER RESULTS

A. Canonical Ensemble

Having completed the theoretical basis for these computations, let us now consider the results. The computer programs have been written to allow the maximum flexibility. We can independently and arbitrarily vary the number of particles, cells, and potential, and the temperature of the system. We can also vary the diameter of the particle to whatever value we choose. Variation of the particle diameter which we have called e has the effect of increasing the fineness of our grid and leads to more of the phenomena of the continuum.

The calculations we have made were on systems of small size 7 particles or less. Larger systems require lengthy computer calculations and such long calculations were not deemed necessary to see the results. The potential we examine first is of the Lennard-Jones type $V(x) = 100[(\frac{2}{x})^{12} - (\frac{2}{x})^{6}]$. $V(1) = +403{,}200$ and hence for all practical purposes as far the computer is concerned $e^{-\beta V_1} = 0$ meaning that configurations in which particles occupy adjacent cells are not allowed. Thus we take e = 2. We first consider a system containing 5 particles and examine its statistical behavior. We first check the correlation function. It has been computed for systems of from 13 to 24 cells and reveals much about the behavior of these systems. Figures 3, 4, and 5 contain the plots of correlation function versus separation of particles. We previously showed that $\mathrm{cor}(k) = \frac{N}{n^2} \langle P_n \rangle$ where P_k is the kth component of the profile vector $\overline{P}$. We have added to the profile vector a component P_o which is found as below

$$P_o = \sum_{j=1}^{N} \sigma_j^2 .$$

The definition of P_o is consistent with the form found previously for P_k for $k \neq 0$ in terms of particle occupancy. Since we have chosen hard core type potentials the occupancies are restricted to be either 0 or 1. This implies that $\sigma_i^2 = 0$ or 1 for all $i \leq N$. Since there are n particles in the system, this means that $P_o = n$. We define therefore $\mathrm{cor}(0) = \frac{N}{n^2} \langle P_o \rangle = \frac{N}{n}$ and take cor(0) as the correlation of a particle with itself. It is apparent that there can be no higher correlation than that of a particle with itself, hence $\mathrm{cor}(k) \leq \mathrm{cor}(0)$. If the equality holds, we have perfect correlation. This can also be seen by noting the form of P_k

$$P_k = \sum_{j=1}^{N} \sigma_j \sigma_{j+k}$$

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]: e = 2, \ T = 1°$

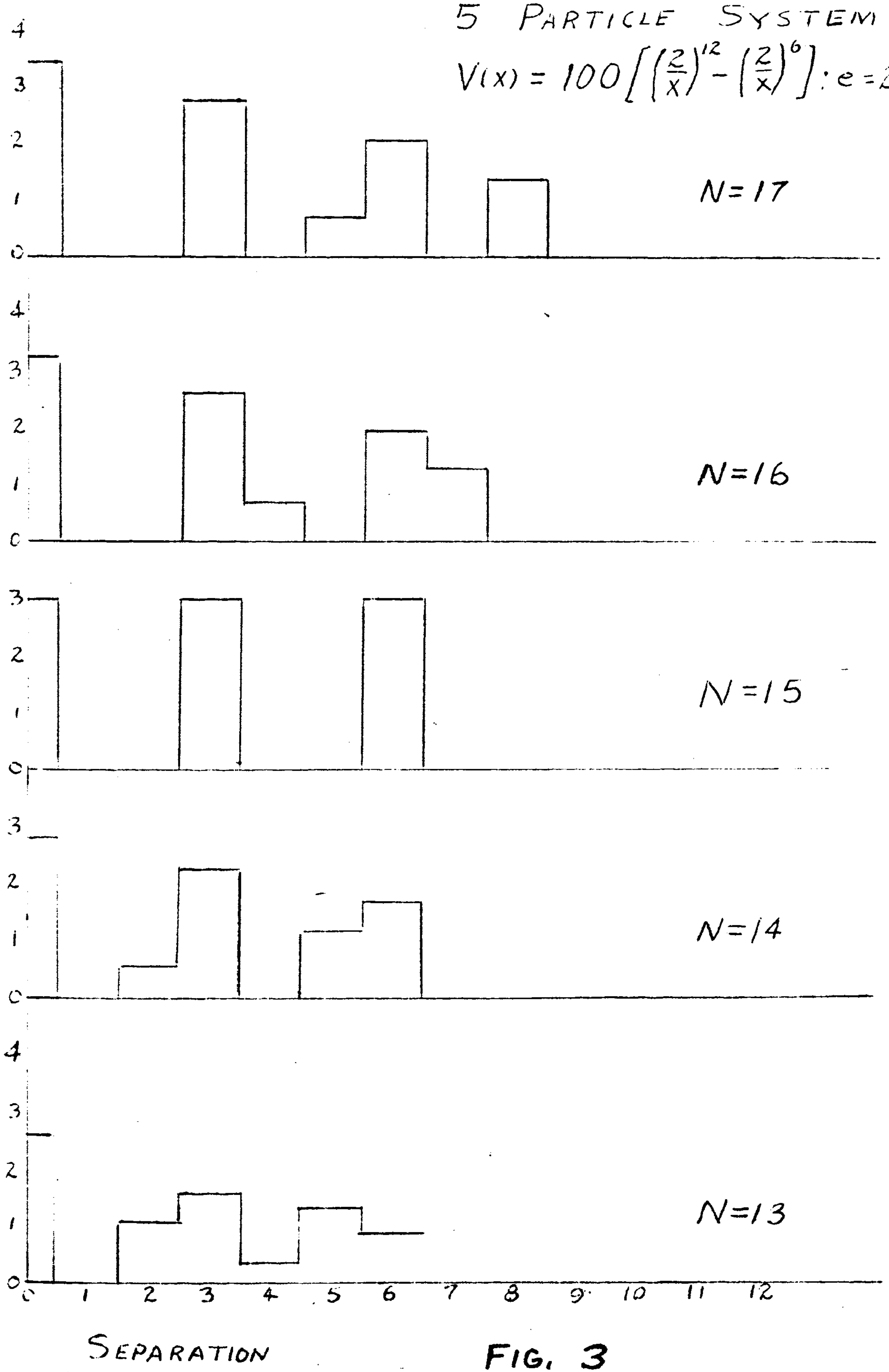
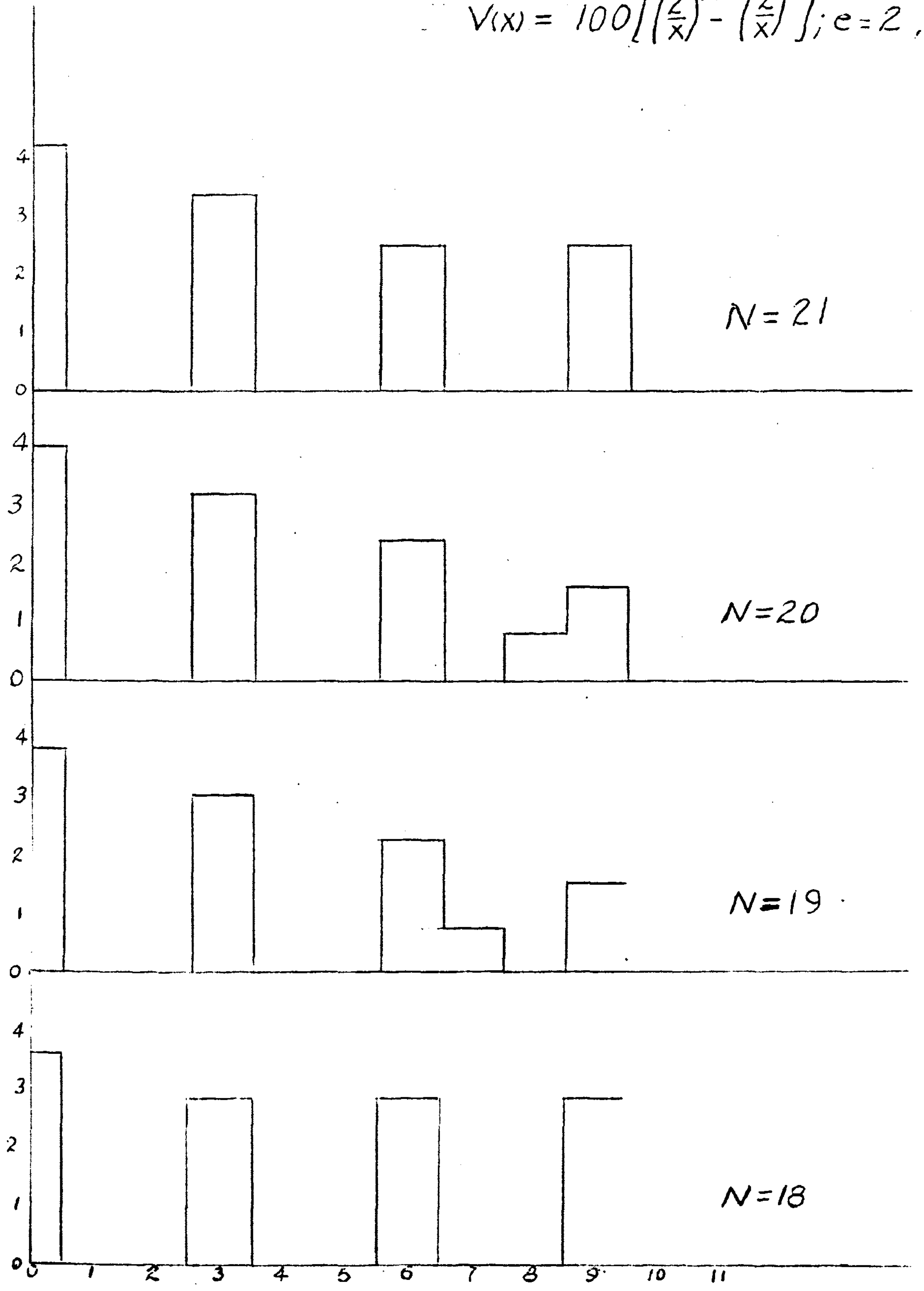


FIG. 3

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e = 2, T = 1°$



SEPARATION

FIG. 4

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $e = 2$, $T = 1°$

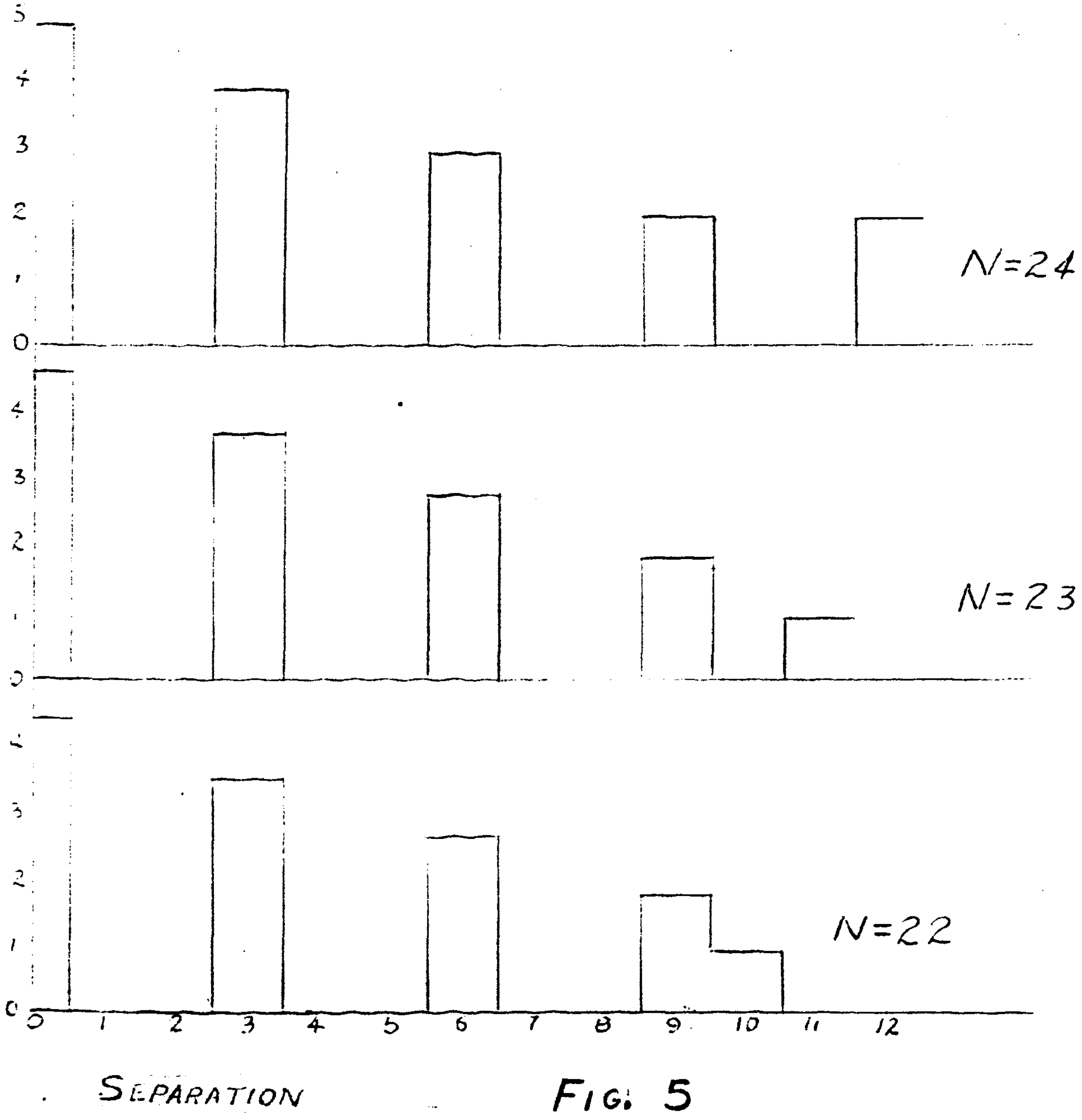


FIG. 5

n of the σ_j's are nonzero and hence no more than n of the products $\sigma_j\sigma_{j+k}$ can be nonzero. If $P_k = n$, then whenever $\sigma_j = 1$, $\sigma_{j+k} = 1$ also. Thus $P_k = n$ for perfect correlation at separation k. From Figure 3 we notice the progressive tendency to ordered structure of the correlation function as N varies from 13 to 15. Beyond 15 notice that the peaks at 3 and 6 remain present although of varying heights even through N = 24. This suggests to us a regular structure with particle separations of 3 or 6 occurring often. Mention should be made of the fact that cor(k) = cor(N - k) so that only values for $k \leq N/2$ need be plotted. This is shown by recalling Equation (9) where we found that $P_j = p_j + p_{N-j}$. If we replace j by N-j, we obtain

$$P_{N-j} = p_{N-j} + p_{N-(N-j)} = p_{N-j} + p_j = P_j \Rightarrow \text{cor}(N-j) = \text{cor}(j).$$

At N = 18 we note an additional peak at a separation of 9 further confirming the regularity of the "average" structure. This follows along with the previous results for if separations of 3 and 6 occur often, separations of 9 must also. The graphs of Figures 4 and 5 continue to show peaks at 3, 6, and 9 until at N = 24 a peak forms at 12. We shall discuss this curious result later in our discussion of results.

Next let us examine the behavior of particle correlation with increasing temperatures. Figure 6 shows these results plotted for N = 15, the value of N in which strongest correlation is observed. Note that as T grows

CORRELATION FUNCTION VS TEMPERATURE

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right];\ e=2$

5 PARTICLE SYSTEM, N= 15

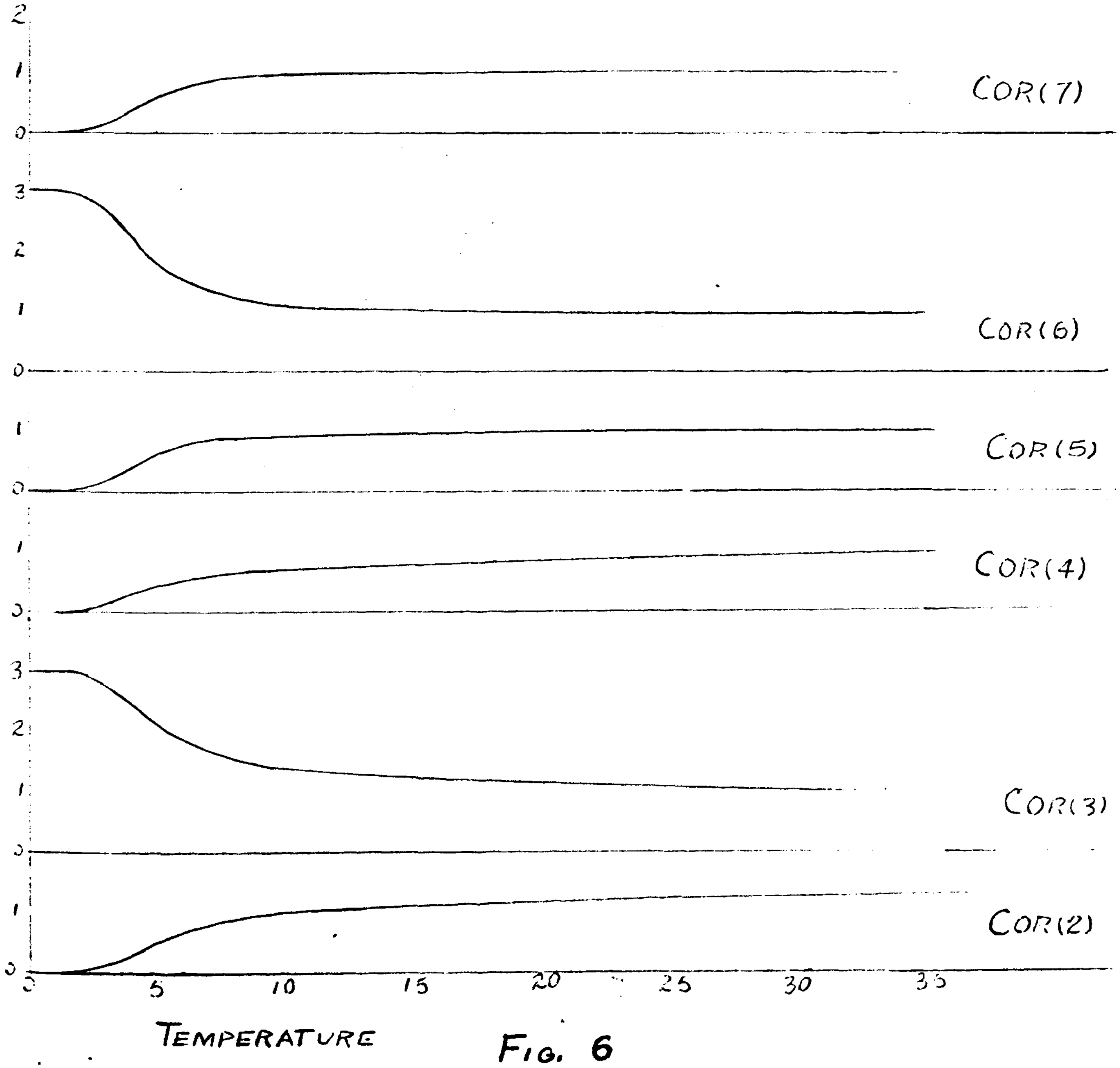
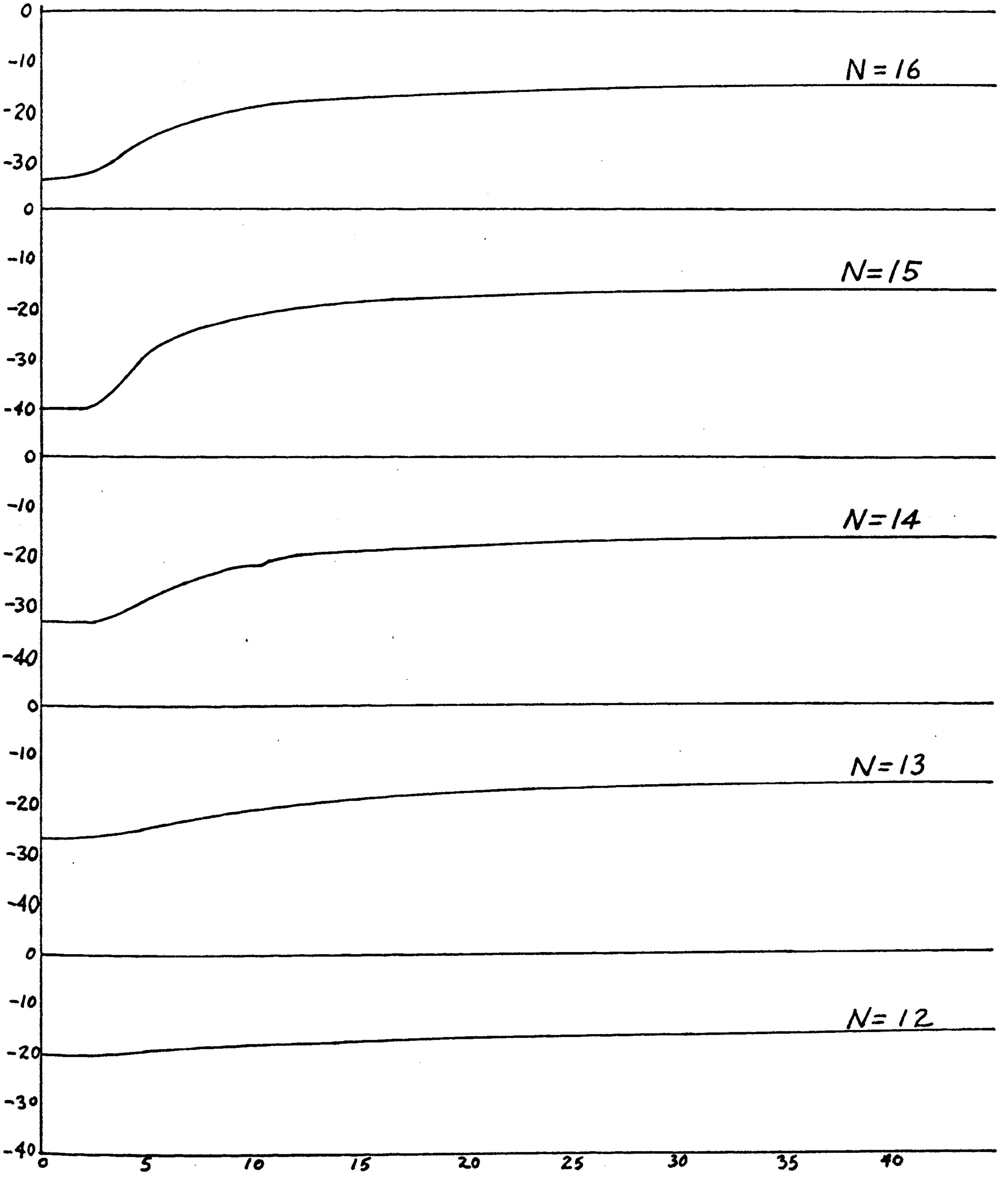


FIG. 6

large all values of the correlation function approach the random correlation values approximately 1. In all cases the major decay of the correlation takes place in the interval from 2° to 10° approximately a fact we should bear in mind when we examine the other thermodynamic functions.

Figure 7 shows the behavior of the internal energy as a function of temperature for the various situations from N = 12 through N = 16. The curves plotted in Figures 7, 8, and 9 are not truly the total internal energy E but only the configurational part. The kinetic energy of the particles contributes a known nkT/2 amount of energy to E so that all of the interesting information is in the average of the interaction energy u. Thus we show the results of <u> versus temperature. Notice that for N = 12 the curve is quite flat changing only slightly. As N increases the change in <u> increases until at N = 15 it is considerable changing by roughly a factor of 2. A close examination of Figures 7, 8, and 9 will reveal that <u> goes the lowest for N = 15 in the neighborhood of -40 for $T \rightarrow 0$. Again note that most of the change takes place between 2° and 10°. The similarity of these curves with those in correlation function versus temperature suggest a connection. We shall show such a connection later and comment on its meaning.

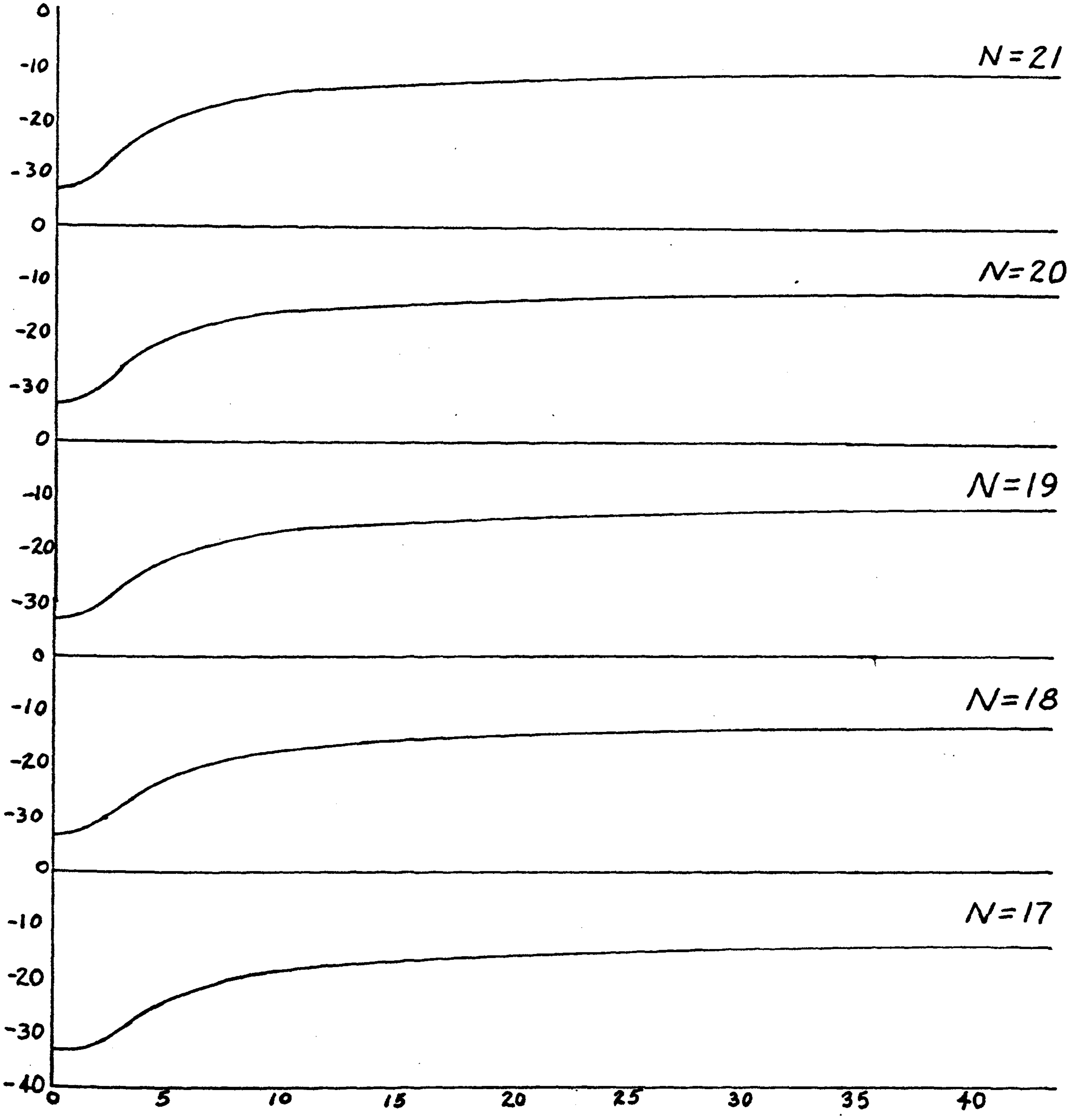
The heat capacity for a system is given by the temperature derivative of the internal energy. Thus



INTERNAL ENERGY VS TEMP.

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e = 2$

FIG. 7



INTERNAL ENERGY ⟨U⟩ VS TEMP.

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e = 2$

FIG. 8

INTERNAL ENERGY ⟨U⟩ VS TEMP.

5 PARTICLE SYSTEMS

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e = 2$

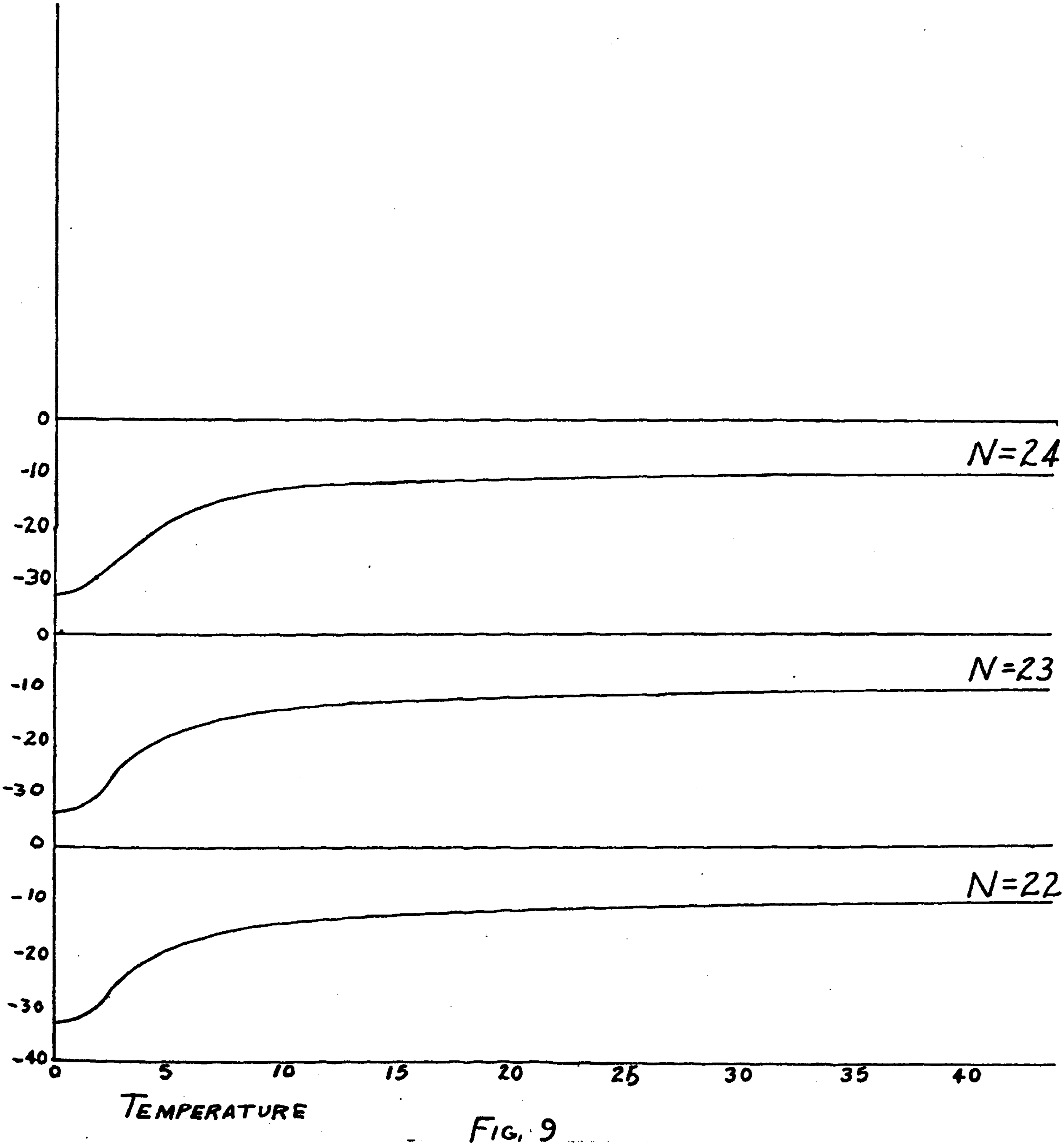


FIG. 9

$$C_v = \frac{n}{2}k + \left(\frac{\partial\langle u\rangle}{\partial T}\right)_N \tag{54}$$

The derivative in (54) is to be evaluated while N is fixed. Thus the curves for the heat capacity consist of a constant part nk/2 plus a part which is just the slope of a curve from Figures 7, 8, or 9. Figure 10 shows the results of computer calculations for the 5 particle system for the heat capacity starting at N = 12 through N = 15. For N = 12 we see the presence of two peaks. As N increases to 13 the second peak grows while the first changes little. By N=14 only one peak remains. For all values of N larger than N = 14 there is the one major peak in the neighborhood of 3 to 4 degrees. Again, we note that C_V differs significantly from n/2 = 2.5 for T in the interval $2^\circ \lesssim T \lesssim 10^\circ$ to N = 24. The behavior after N = 14 changes little except that the maximum of the peak seems to occur at lower temperatures as N increases.

Figure 14 where we plot pressure versus number of cells we observe the first truly anomalous behavior in the system. Everything seems all right for N < 15; however, we find that at N = 15 the curve for T = 1° dips below the 0 axis yielding the unusual and highly suspect negative value. There is another anomaly perhaps for N < 15 the pressure for T = 1° is greater than for T = 2° which in turn is larger than the T = 3° values. The

HEAT CAPACITY VS TEMPERATURE

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; \ e=2$

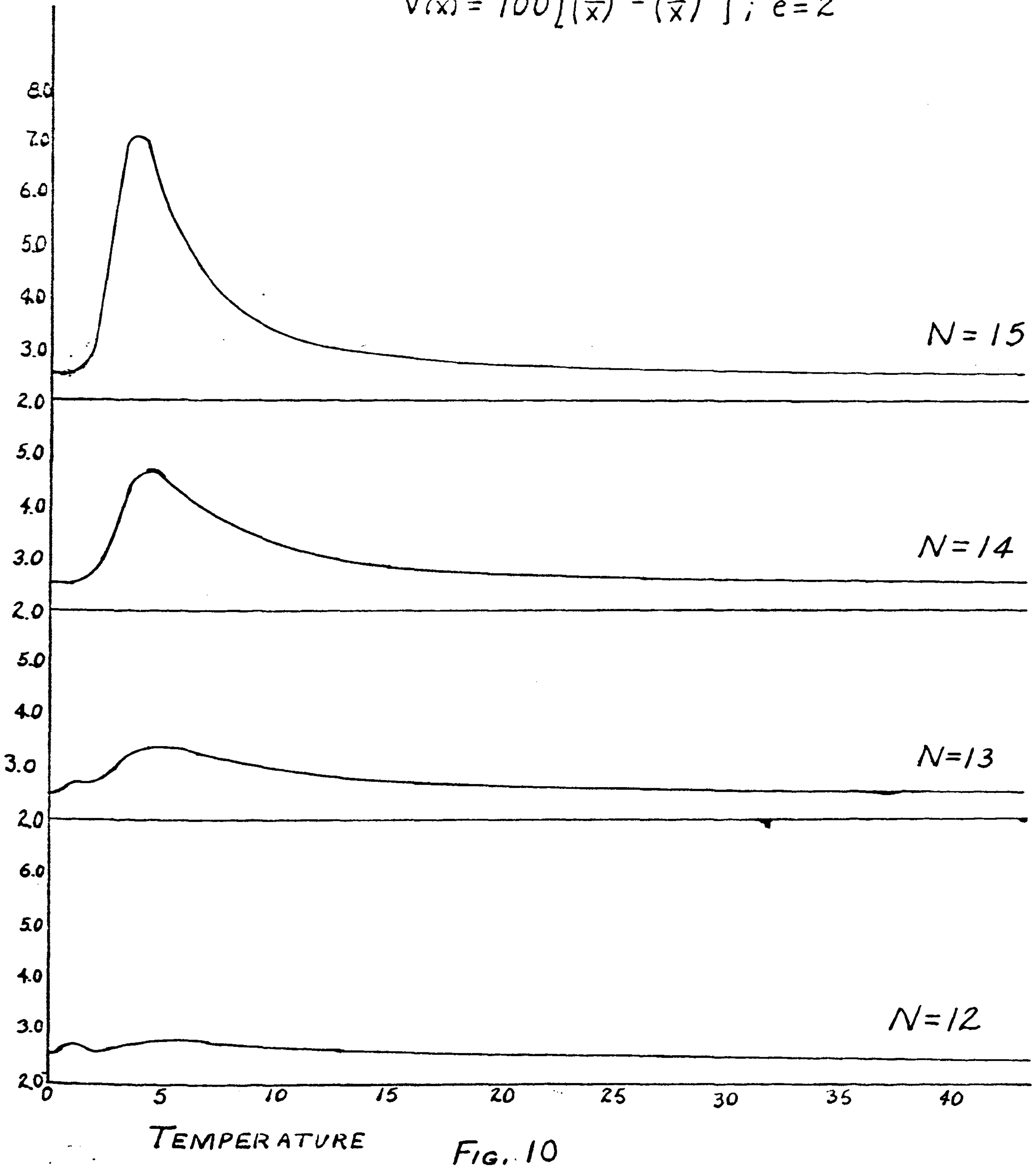


FIG. 10

HEAT CAPACITY VS TEMPERATURE

5 PARTICLE SYSTEMS

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e = 2$

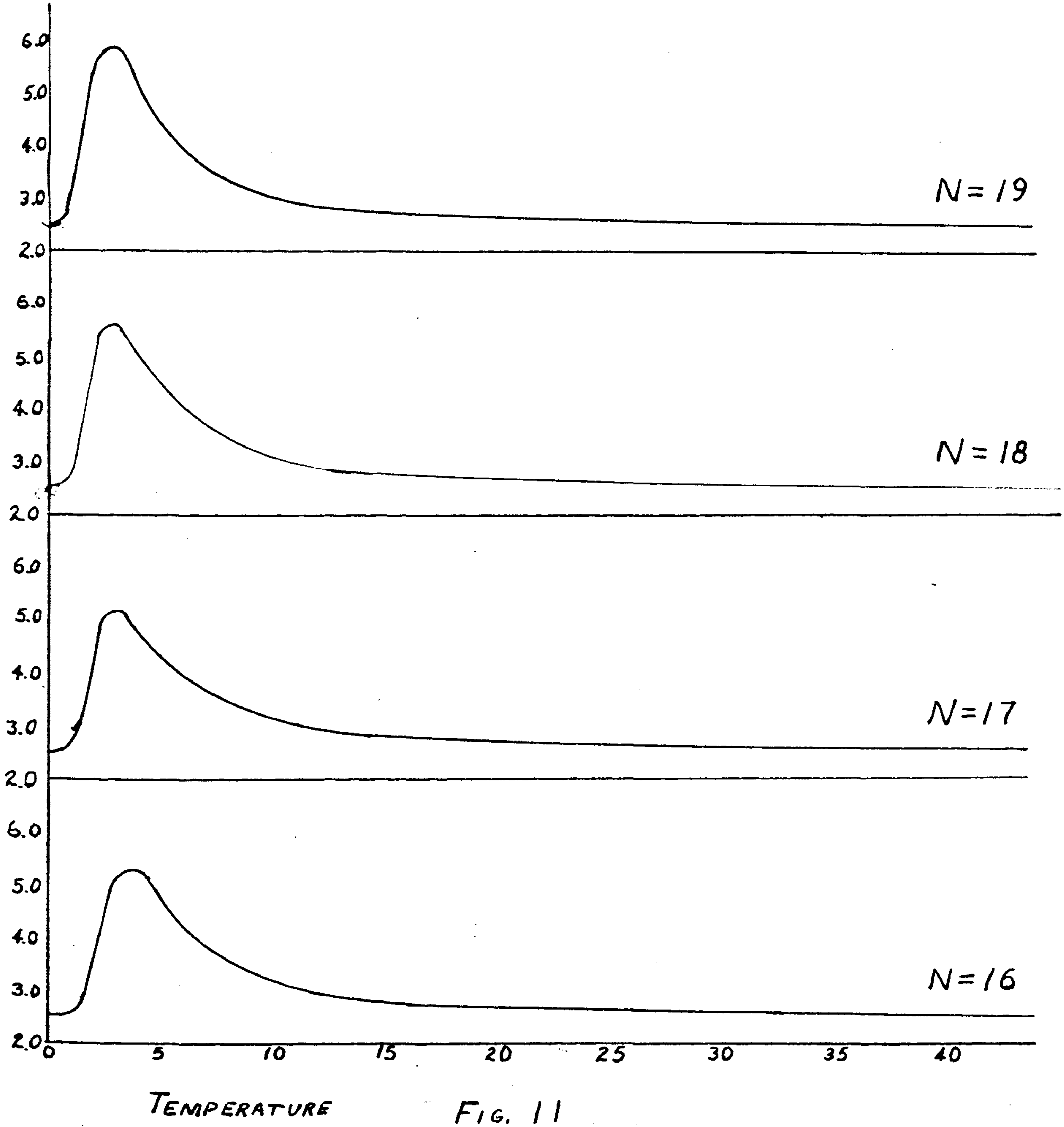
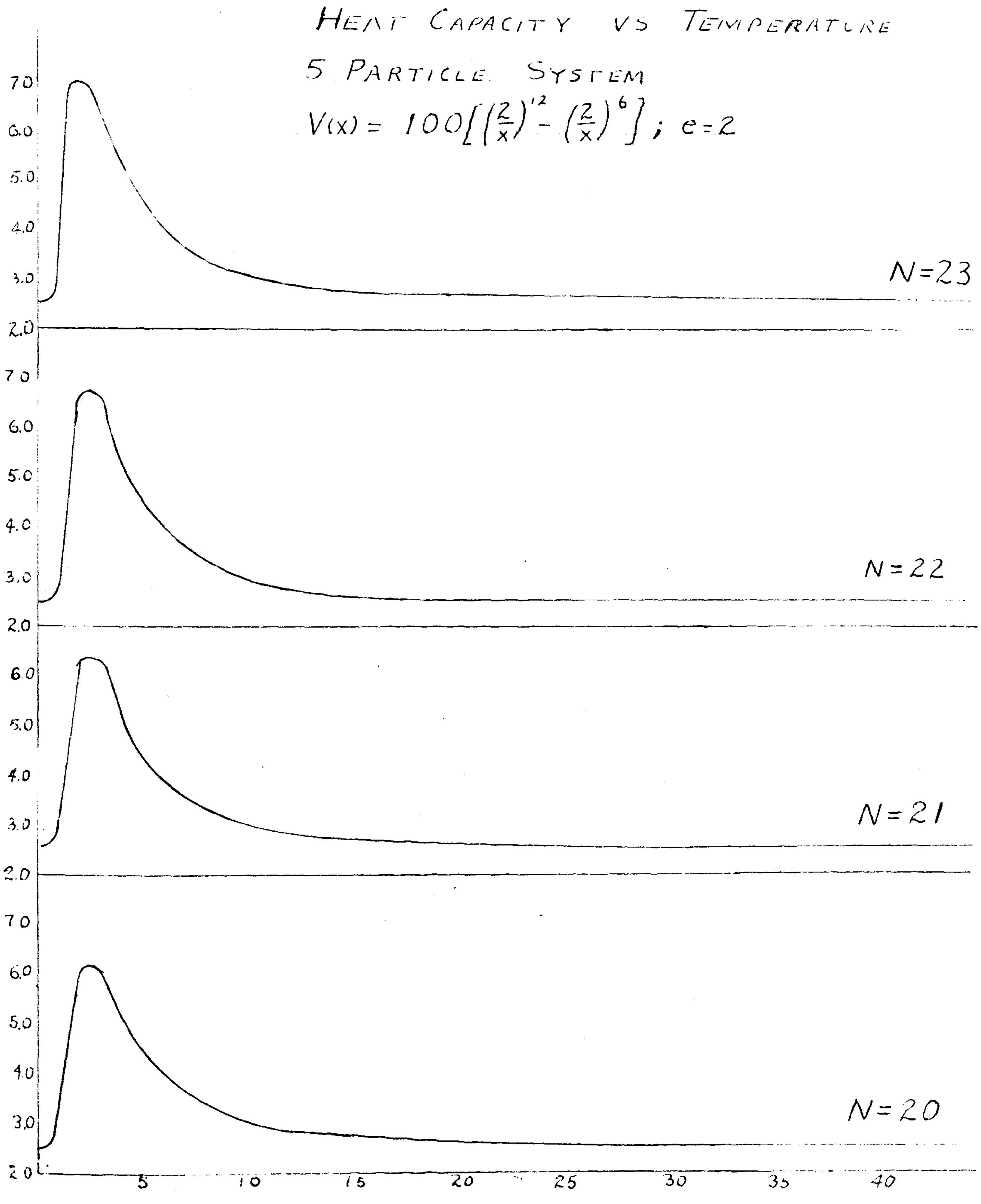


FIG. 11



HEAT CAPACITY VS TEMPERATURE

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $e = 2$

FIG. 12

HEAT CAPACITY VS TEMPERATURE

5 PARTICLE SYSTEM

$V(X) = 100\left[\left(\frac{2}{X}\right)^{12} - \left(\frac{2}{X}\right)^{6}\right]; \; e = 2$

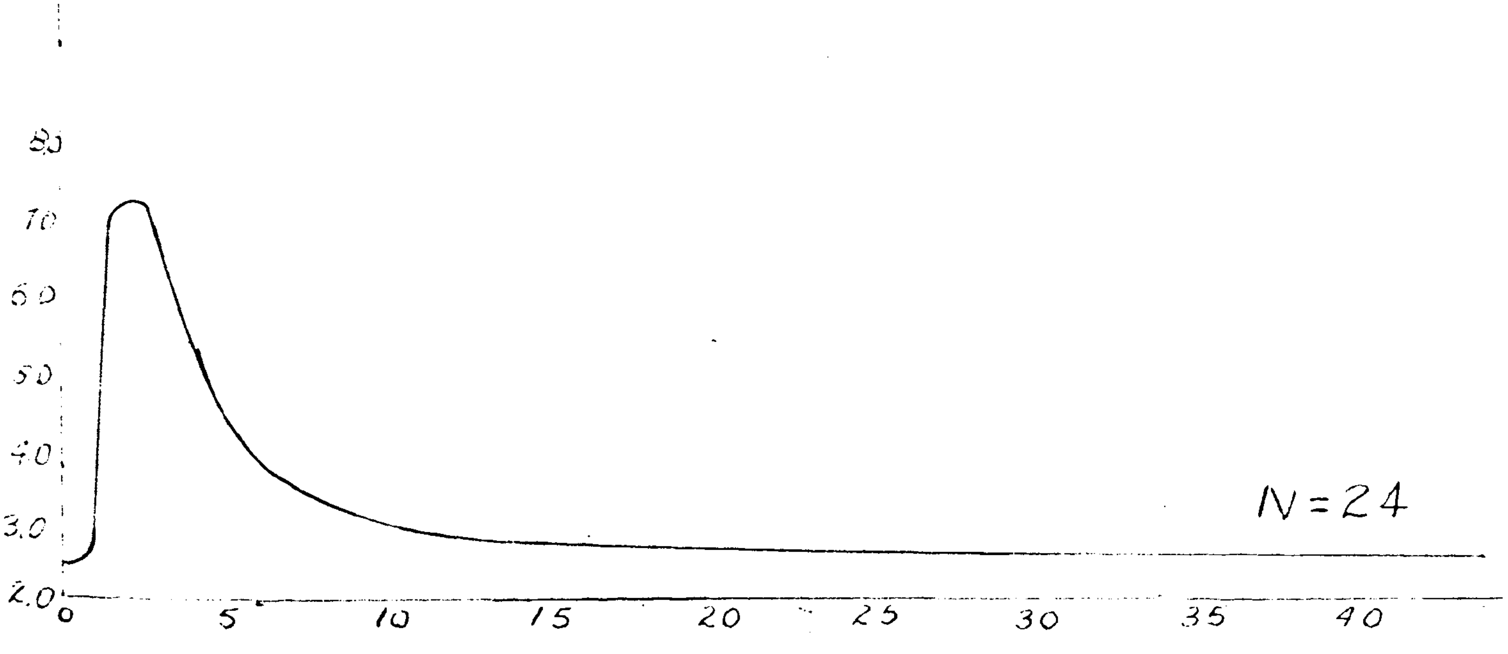
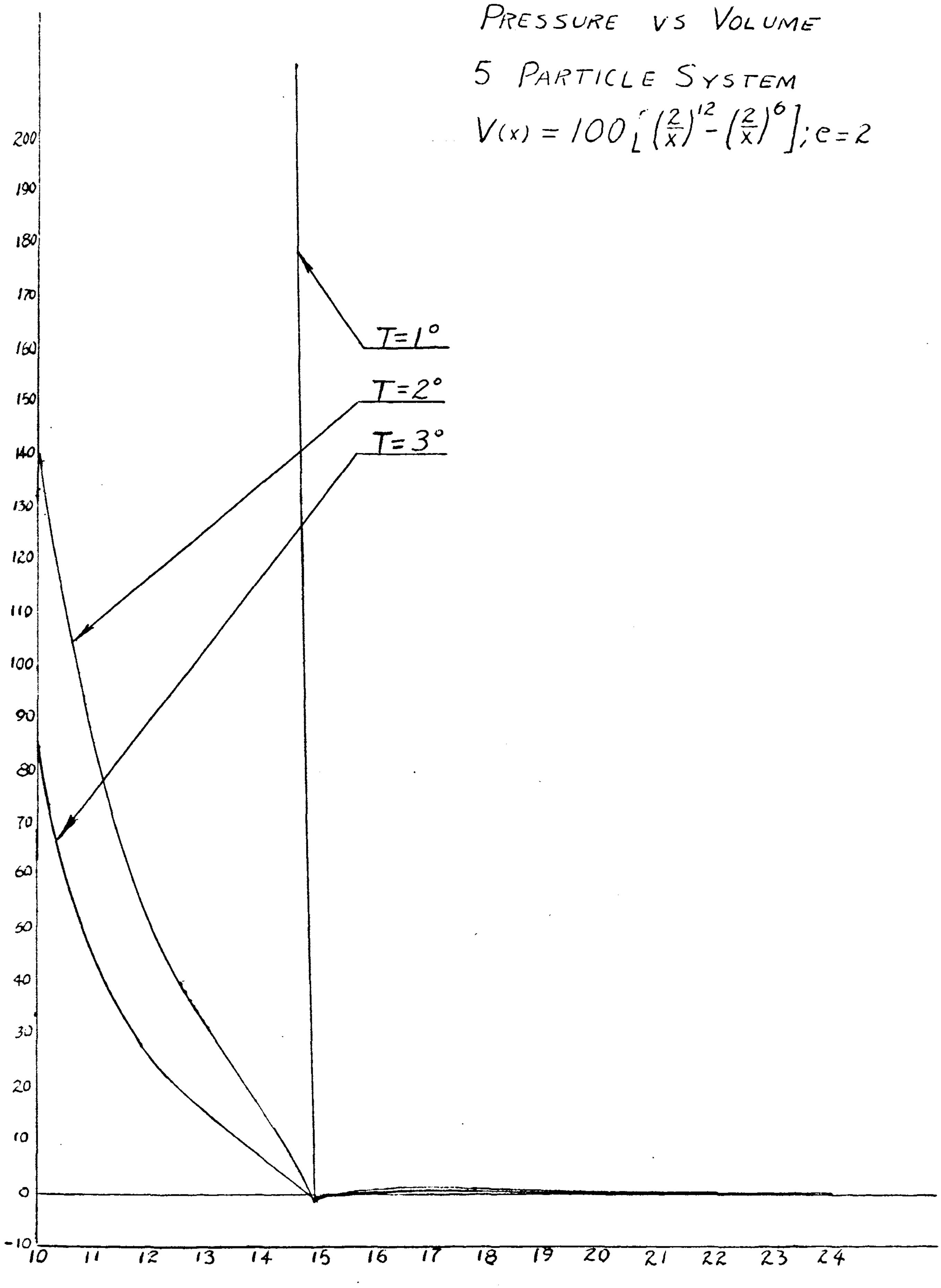


FIG. 13



PRESSURE VS VOLUME

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e = 2$

FIG. 14

negative pressure values may not be so hard to accept if one realizes that in one dimension the pressure is just a force, really the average tension or compression force telling us how much force is required to hold the volume at a particular value. The fact that there are negative values simply means that the system would "prefer" to occupy a smaller volume than the one it is currently in. From the nature of the curves this preferred volume seems to be N = 15. For N < 15 the pressure is positive while for N = 15 and a few larger volumes it is negative. For N in the neighborhood of 19 or 20 the pressure is again positive and decreasing. We shall see later that these results are entirely reasonable. Figure 15 shows more pressure-volume curves for higher temperatures. The results are approaching the more customary pressure-volume curves one is familiar with. Figure 16 shows curves for still higher temperatures, which now look much more familiar to us.

Figures 17 through 27 show the same sort of results computed for a 6 particle system for the same Lennard-Jones potential as used previously. Again note the anomalous pressure-volume curves and the excellent correlation at T = 1° for $N \geq 18 = 3 \cdot 6$. Note that peaks again occur at separations of 3, 6, 9, and 12, etc. This behavior also shows up in results for a 7 particle system shown in Figure 28 which shows how order emerges out of

PRESSURE VS VOLUME

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; e = 2

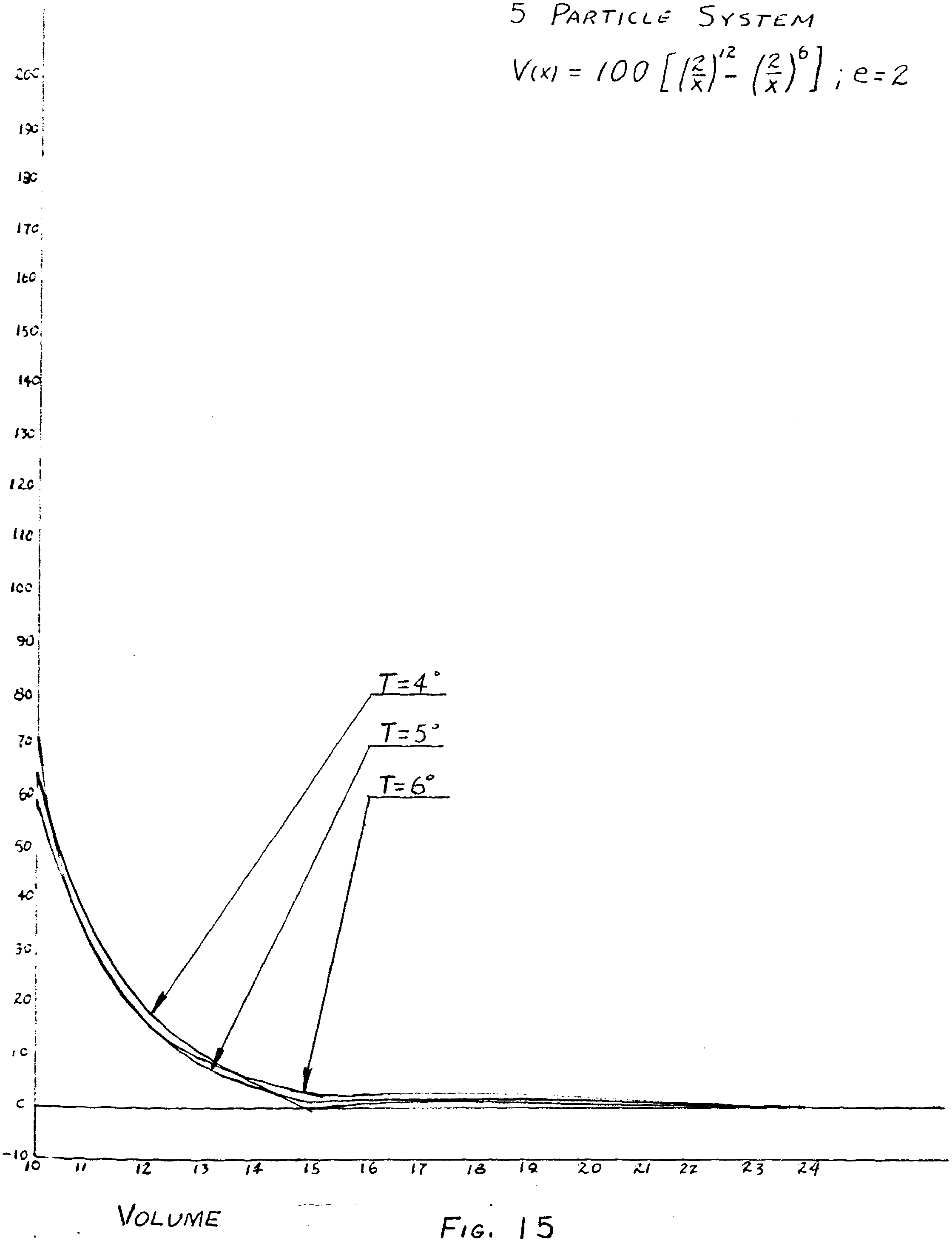


FIG. 15

PRESSURE VS VOLUME

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$, $e = 2$

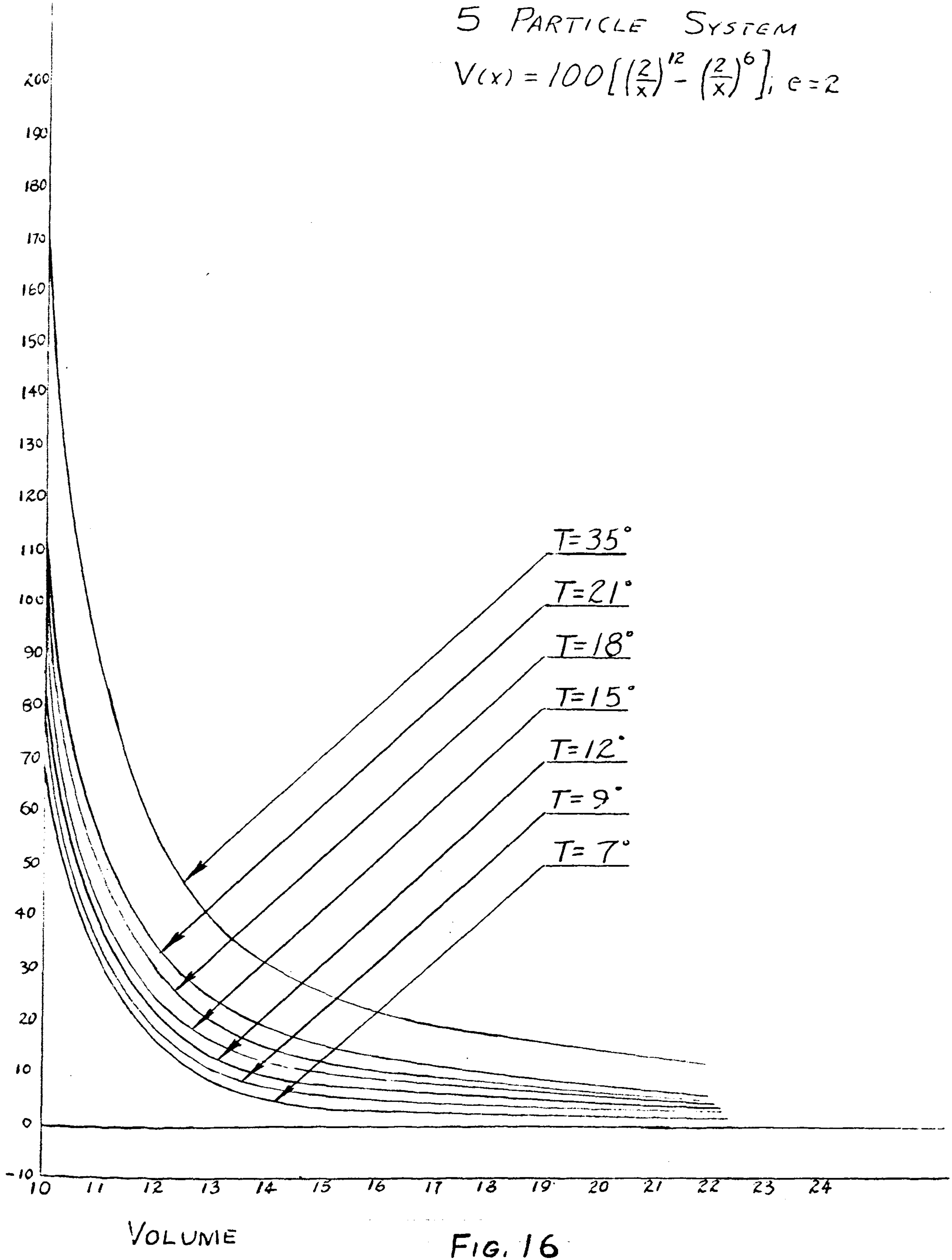
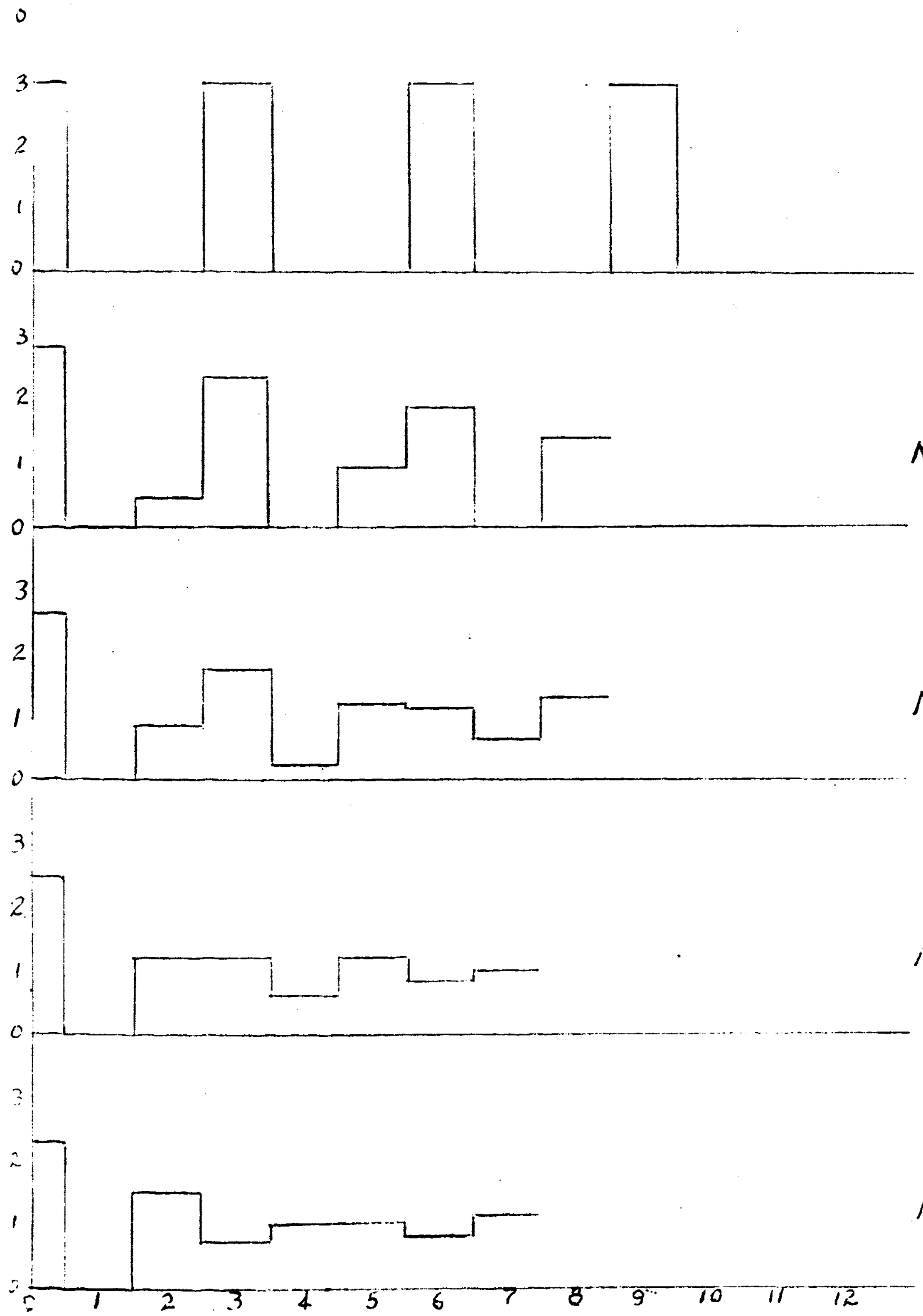


FIG. 16

CORRELATION FUNCTION VS SEPARATION

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $e = 2$, $T = 1°$



SEPARATION

FIG. 17

CORRELATION FUNCTION VS SEPARATION

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $e = 2$, $T = 1^{\circ}$

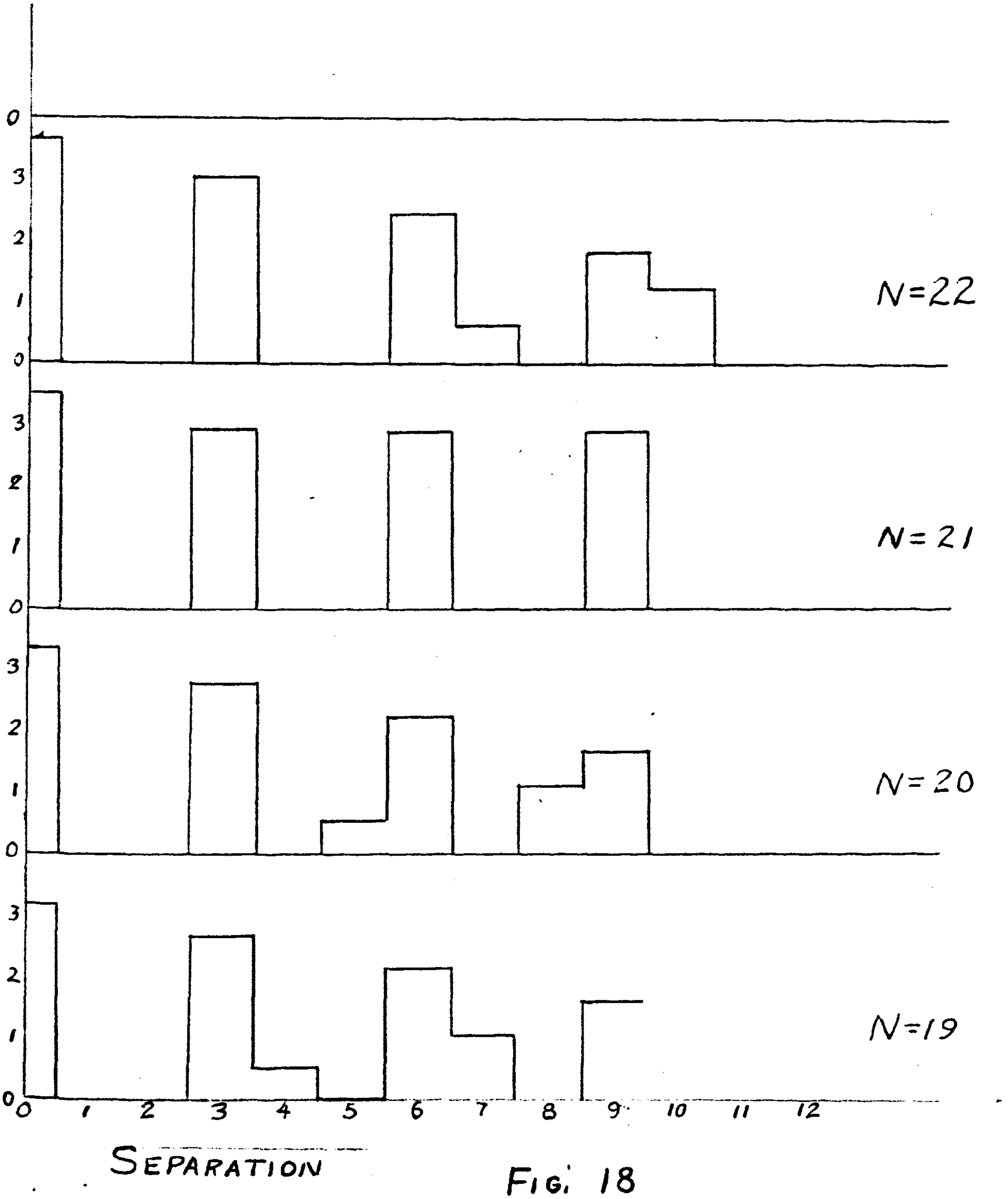


FIG. 18

CORRELATION FUNCTION VS SEPARATION

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $e = 2$, $T = 1°$

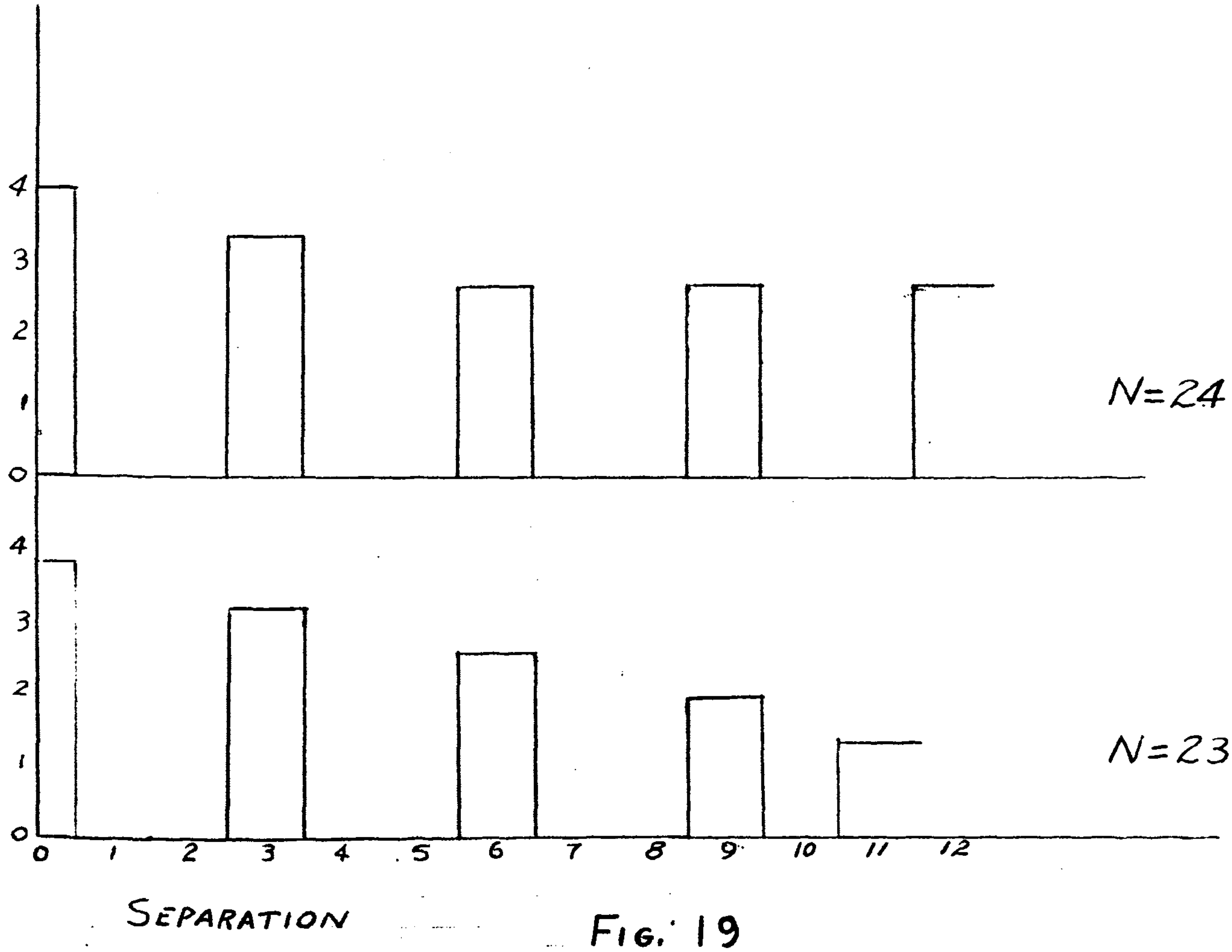


FIG. 19

CORRELATION FUNCTION VS TEMPERATURE

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $e = 2$. $N = 18$

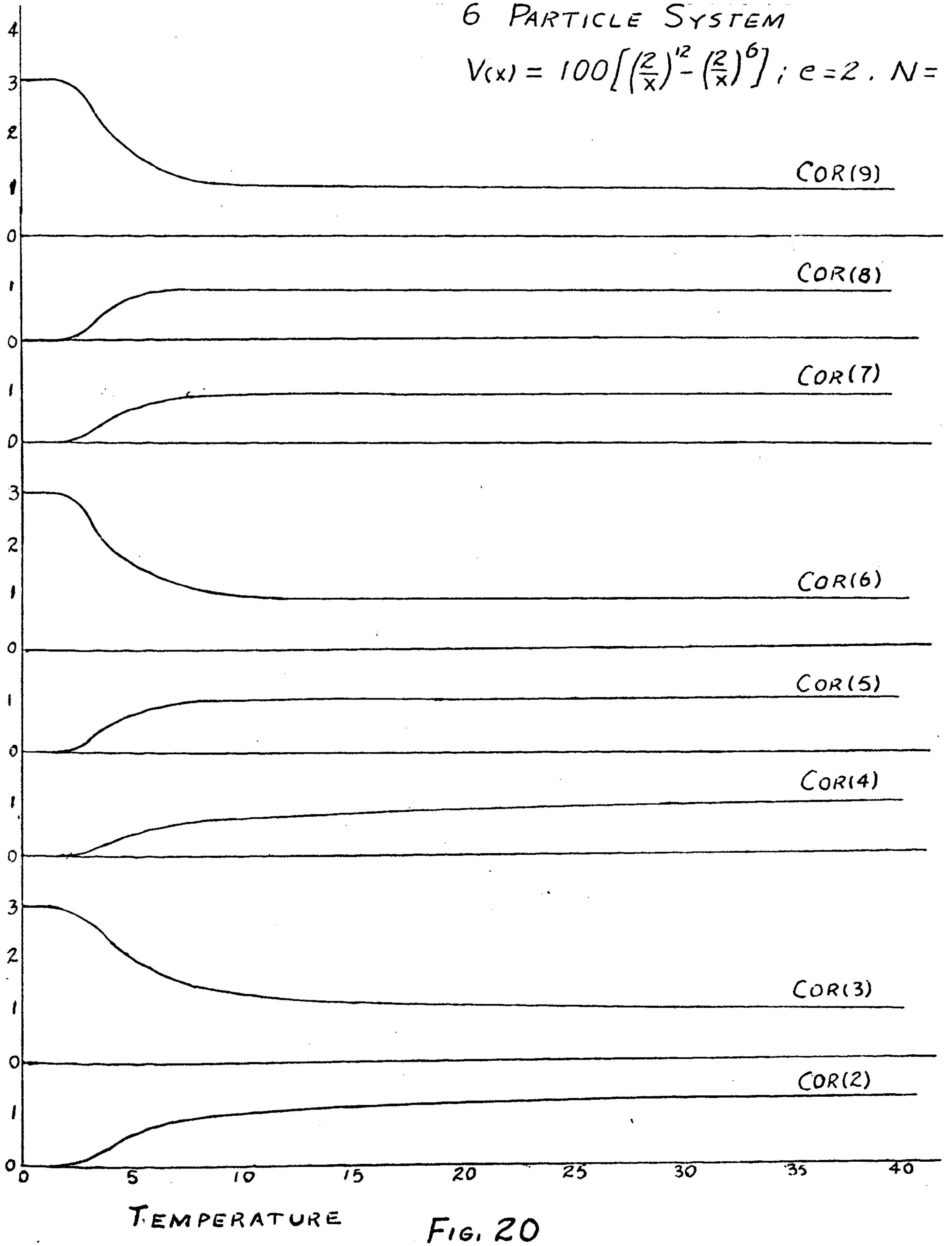
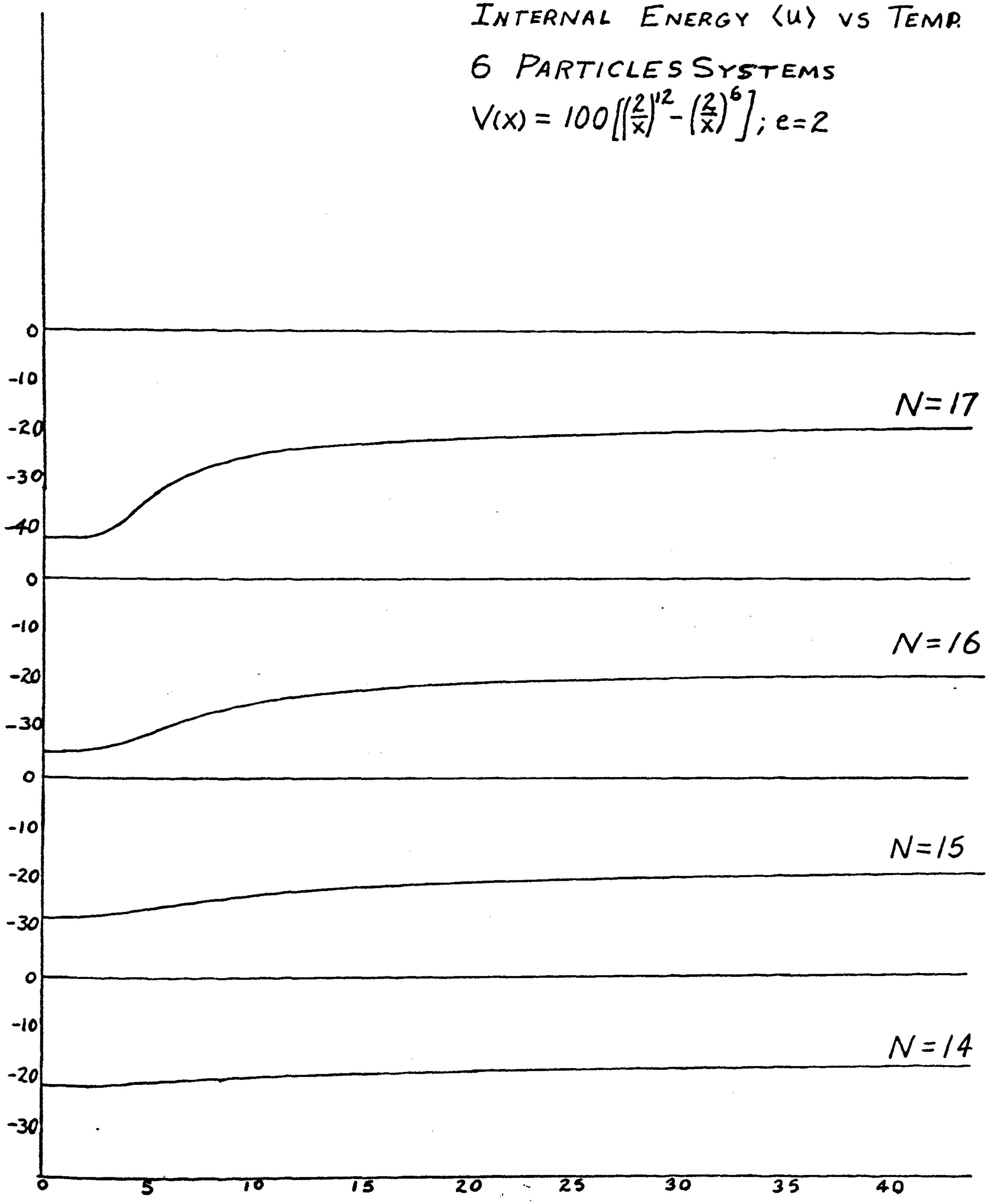


FIG. 20



INTERNAL ENERGY ⟨u⟩ VS TEMP.

6 PARTICLES SYSTEMS

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right];\ e=2$

FIG. 21

INTERNAL ENERGY ⟨U⟩ VS TEMP.

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right];\ e=2$

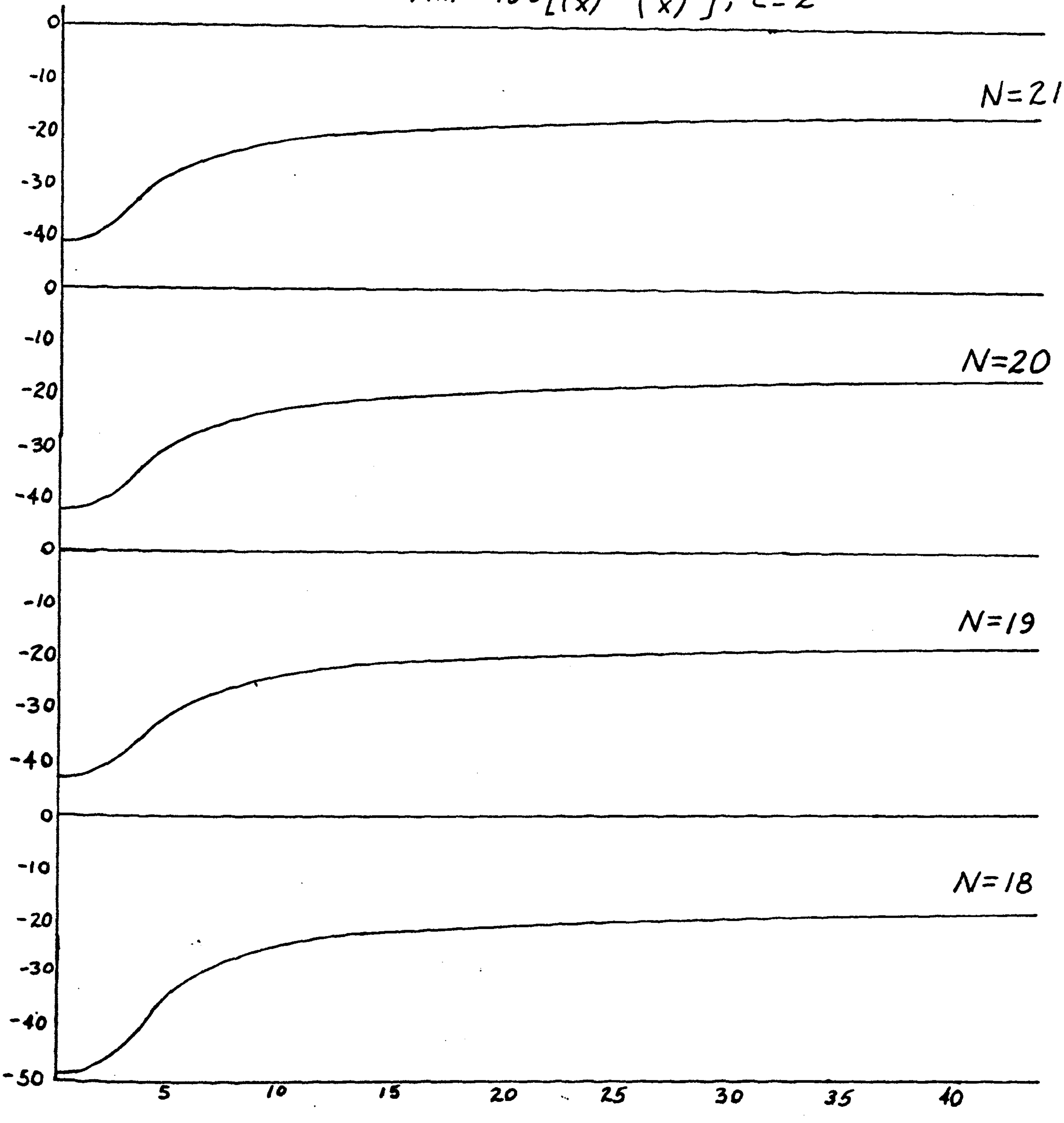


FIG. 22

INTERNAL ENERGY ⟨u⟩ VS TEMP.

6 PARTICLE SYSTEM

$$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right];\ e = 2$$

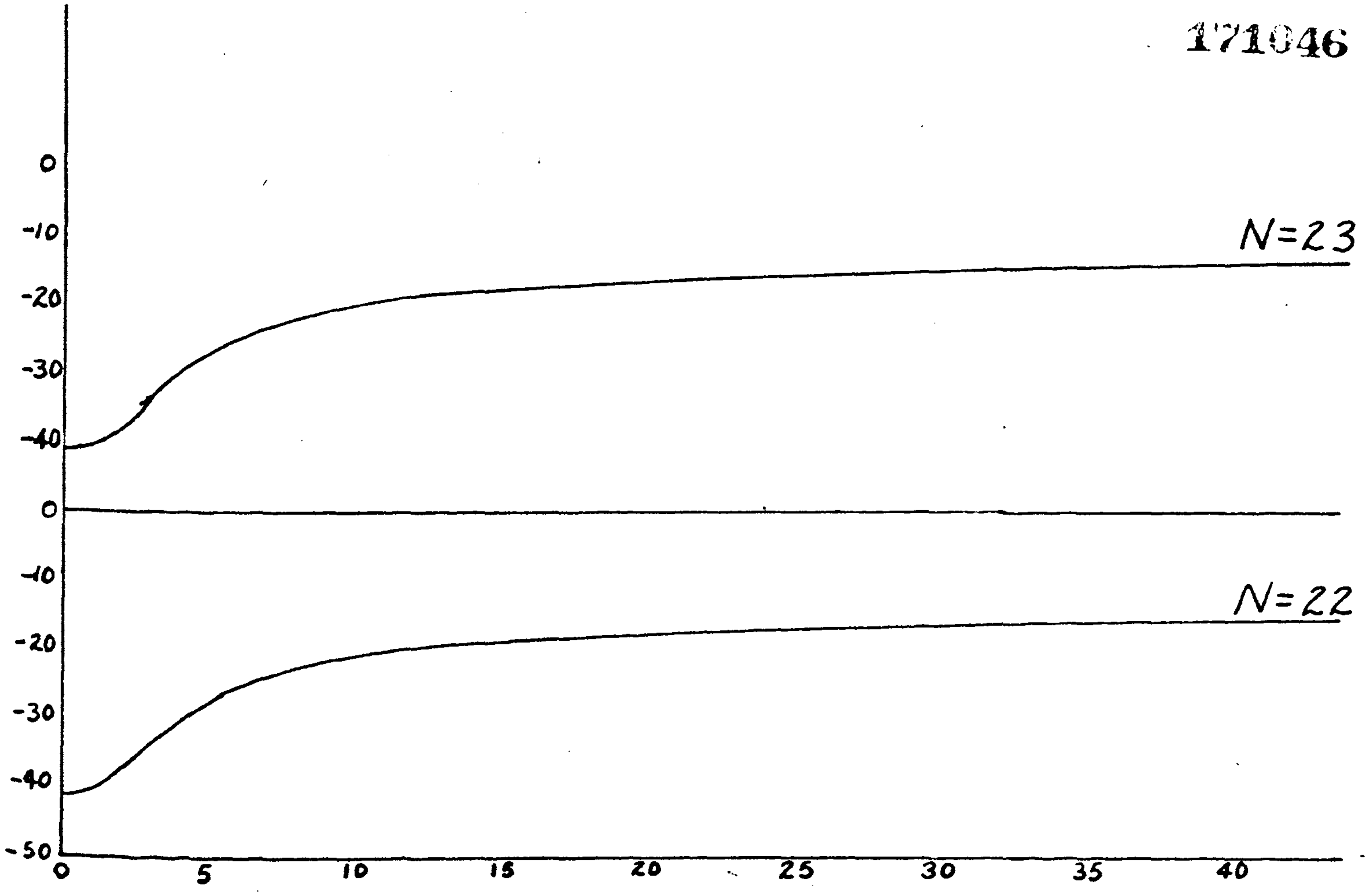


FIG. 23

HEAT CAPACITY VS TEMPERATURE

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e = 2$

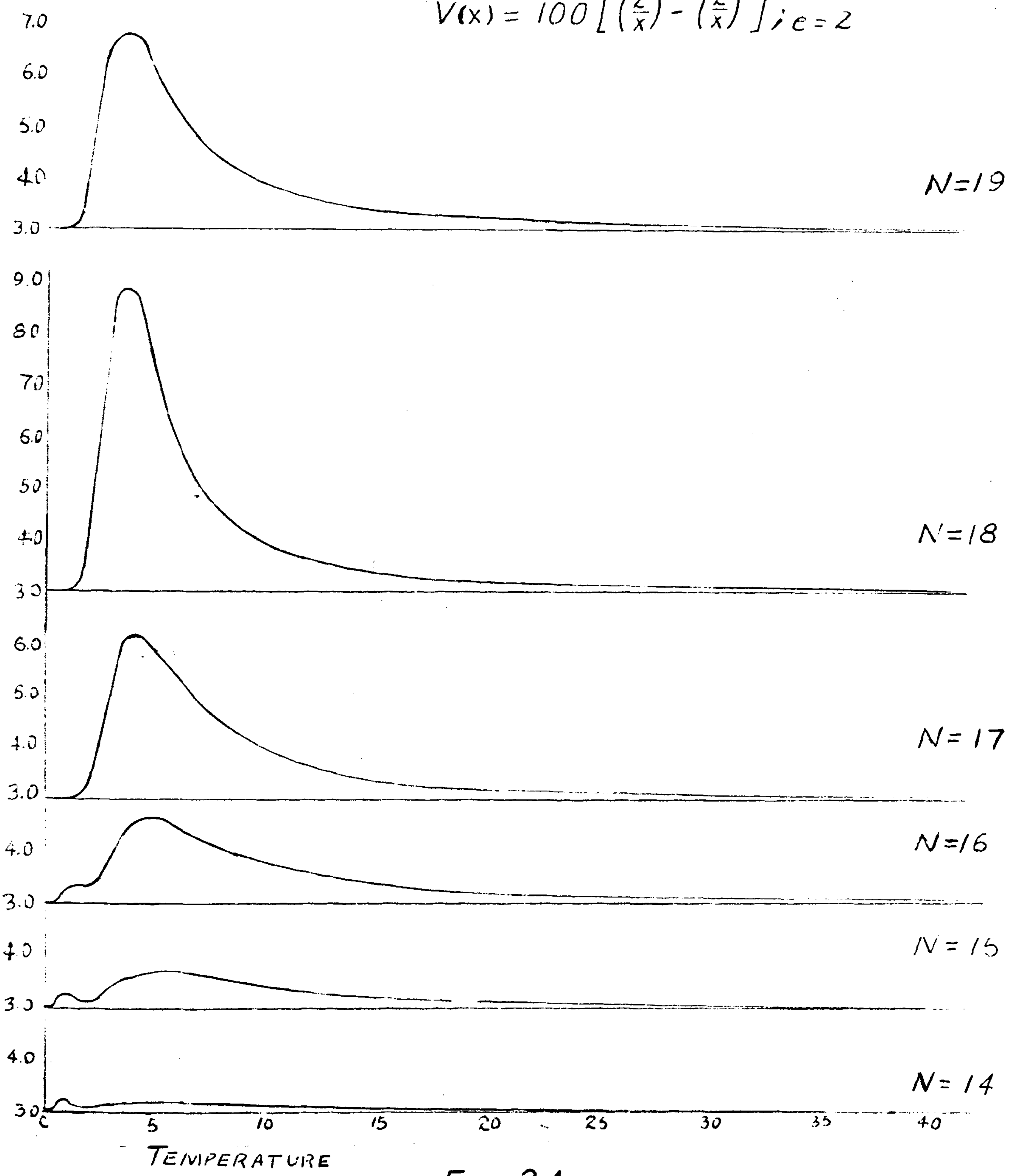


FIG. 24

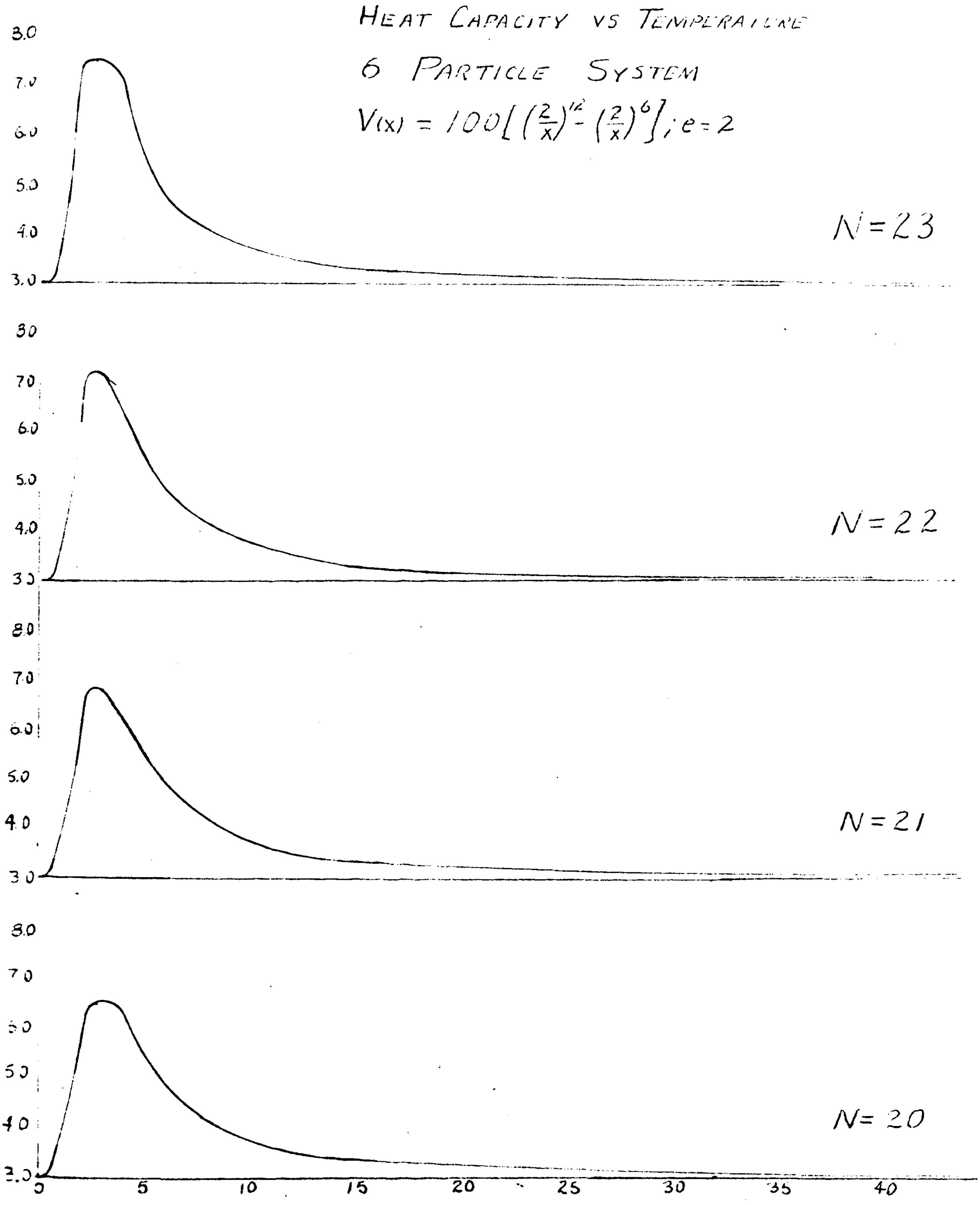
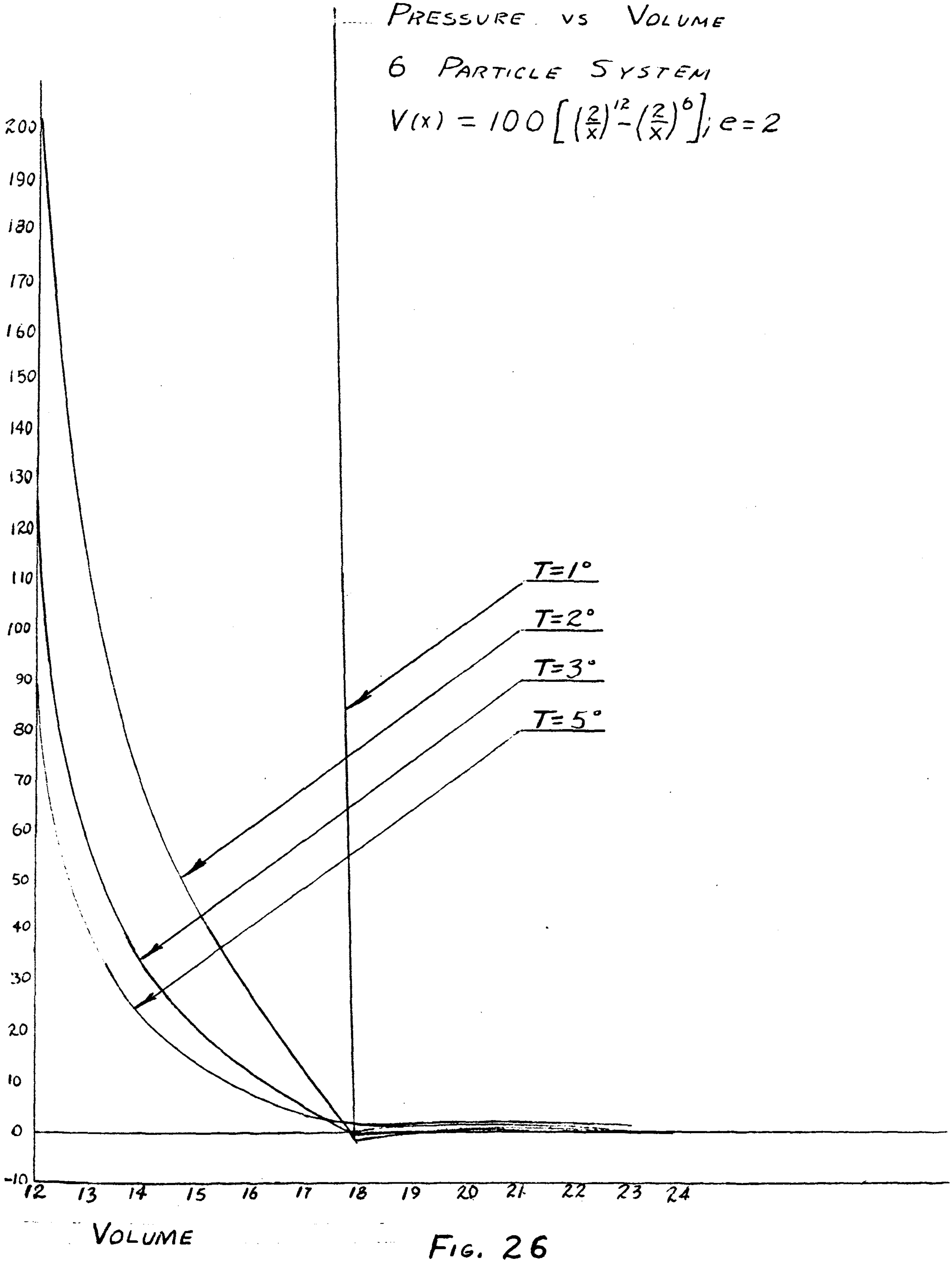

HEAT CAPACITY VS TEMPERATURE
6 PARTICLE SYSTEM
$V(x) = 100[(\frac{2}{x})^{12} - (\frac{2}{x})^{6}]; e=2$
8.0
7.0
6.0
5.0
4.0
3.0
N=23
8.0
7.0
6.0
5.0
4.0
3.0
N=22
8.0
7.0
6.0
5.0
4.0
3.0
N=21
8.0
7.0
6.0
5.0
4.0
3.0
N=20
0
5
10
15
20
25
30
35
40
TEMPERATURE

FIG. 25

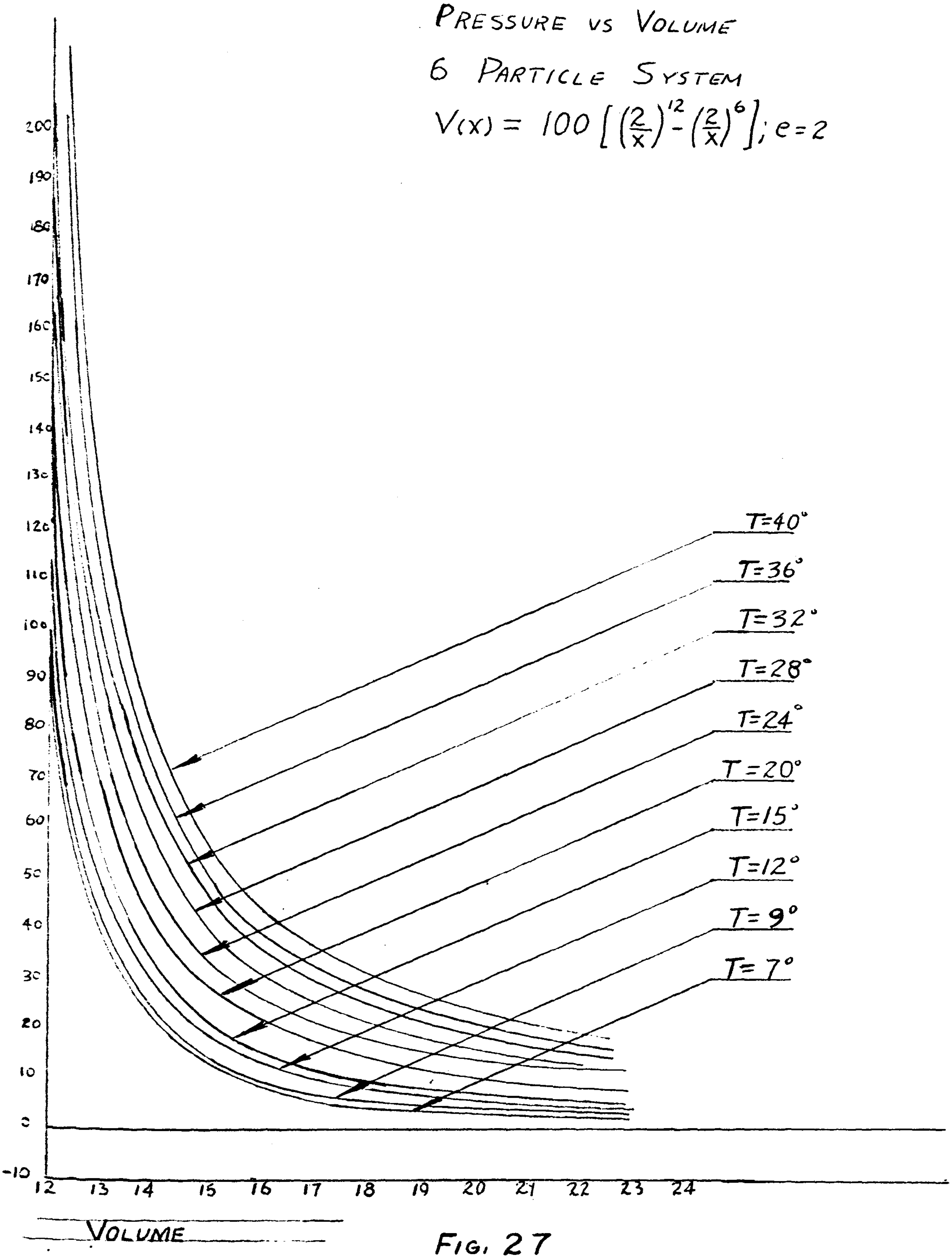


PRESSURE vs VOLUME

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right];\ e = 2$

FIG. 26

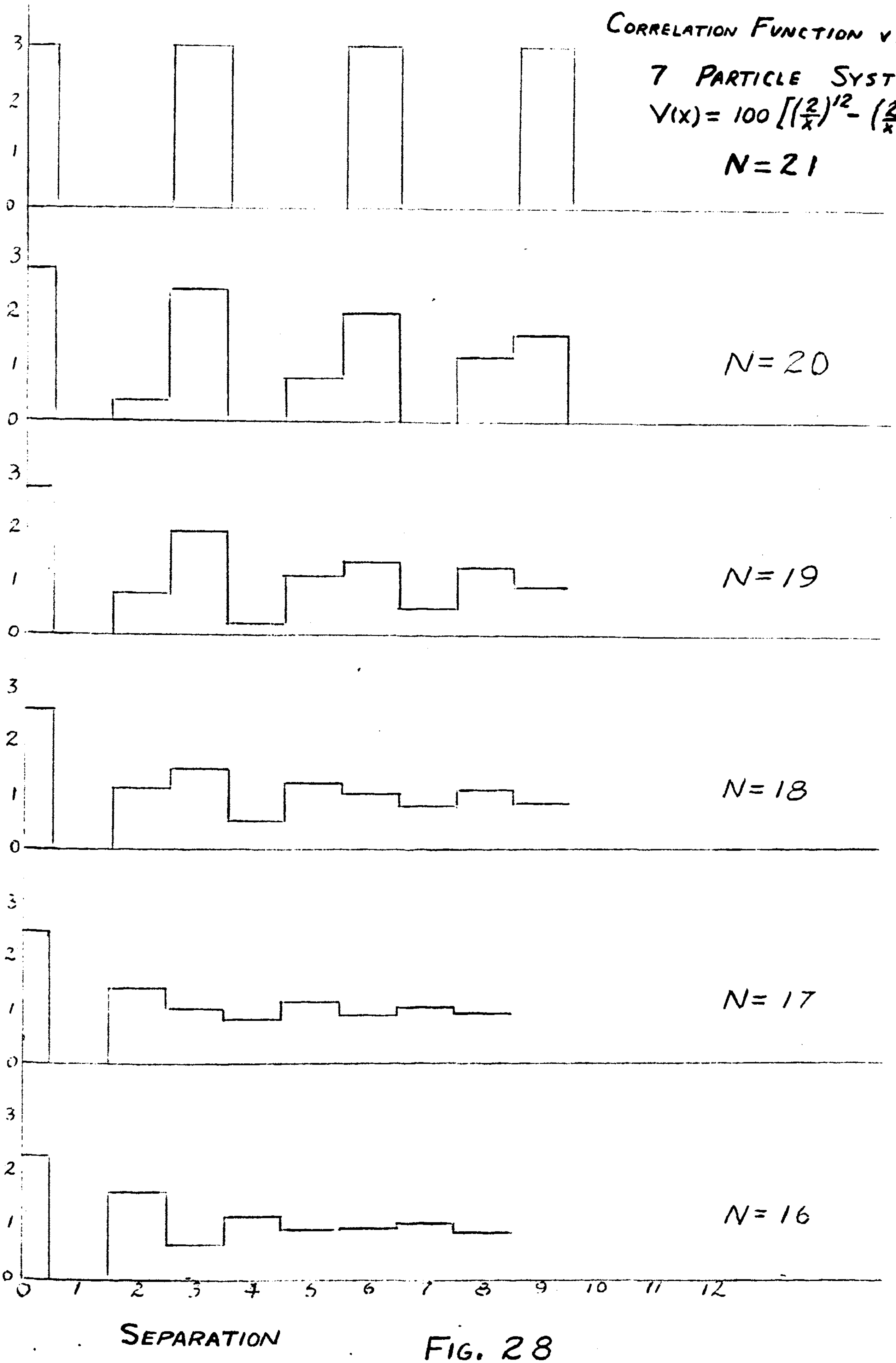


PRESSURE VS VOLUME

6 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]; e=2$

FIG. 27



CORRELATION FUNCTION VS SEPARATION

7 PARTICLE SYSTEM, $e=2$

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $T=1°$

FIG. 28

chaos as N varies from $N = 16$ to $N = 7 \cdot 3 = 21$. Again, when $N = 3 \cdot n$ we have nearly perfect correlation at separations of 3, 6, and 9 cells showing how well-ordered our system is.

Let us look briefly at another Lennard-Jones potential $V(x) = 100[x^{-12} - x^{-6}]$. The heat capacity curves are plotted for various sized systems from $N = 7$ to $N = 15$ in Figures 29 and 30. For $N = 7$ the curve peaks slightly and as N increases to 10 the height of the peak increases with N. It is at maximum height for $N = 10$. For larger N it is somewhat lower. The peak value occurs for temperatures less than 1° indicating that the interaction is not as strong.

Figure 31 shows a set of graphs of correlation function versus separation for a system of 5 particles interacting through the potential

$$V(X) = \begin{matrix} \infty \; ; \; x < 2 \\ -64\left(\frac{2}{x}\right)^6 \end{matrix}$$

This potential is different from the straight Lennard-Jones in that it has no soft repulsive part. It is attractive all the way into the hard core which has a diameter of 2 cells indicating $e = 2$. Thus the strongest attractive interaction occurs at the minimum possible separation 2 cells. We would expect to find much correlation at a separation of 2 cells and perfect anticorrelation for a separation of 1. Figure 31 reveals that this is just the

HEAT CAPACITY VS TEMPERATURE

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{1}{x}\right)^{12} - \left(\frac{1}{x}\right)^{6}\right];\ e = 1$

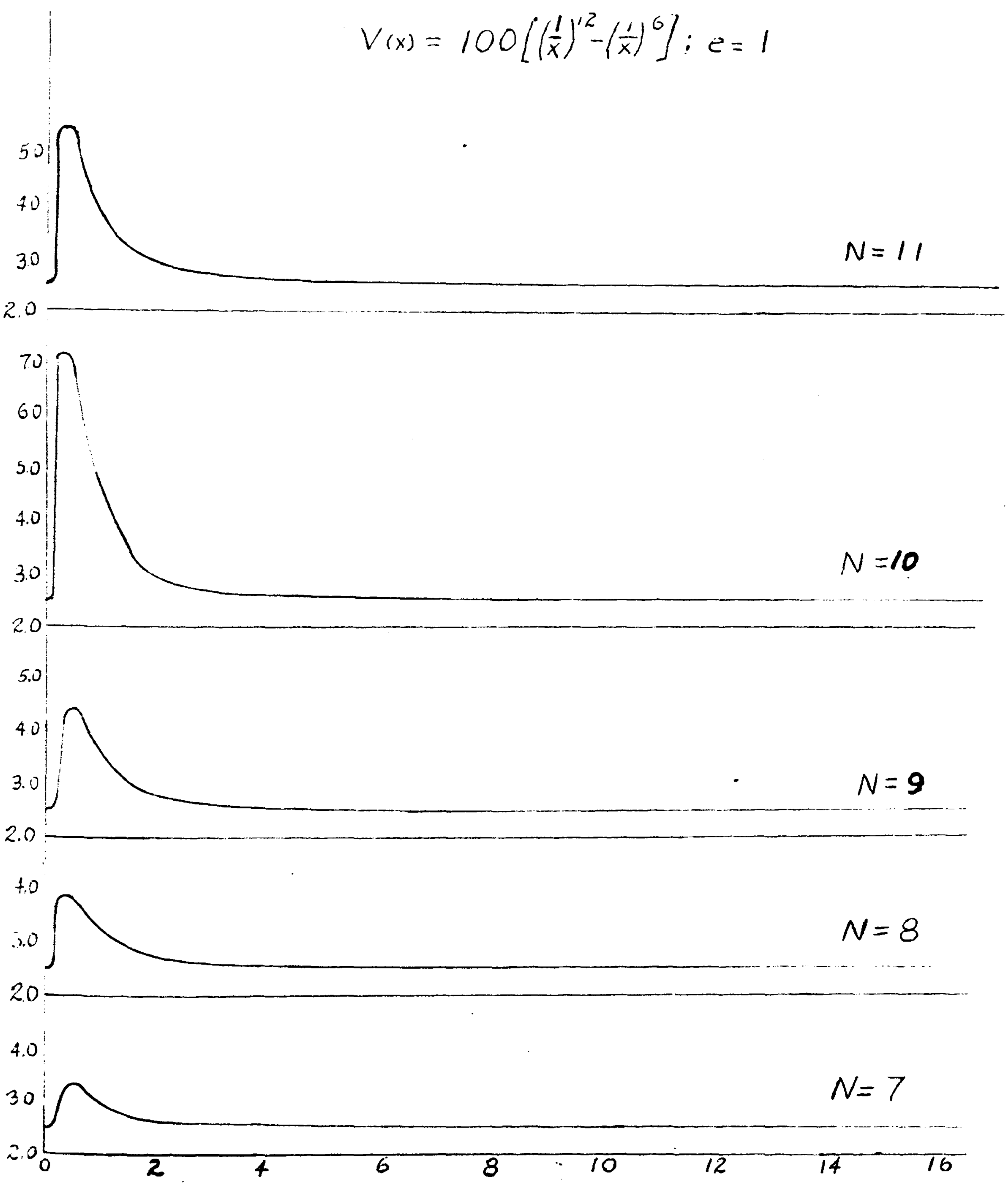


FIG. 29

HEAT CAPACITY VS TEMPERATURE

5 PARTICLE SYSTEM

$V(x) = 100\left[\left(\frac{1}{x}\right)^{12} - \left(\frac{1}{x}\right)^{6}\right];\ e=1$

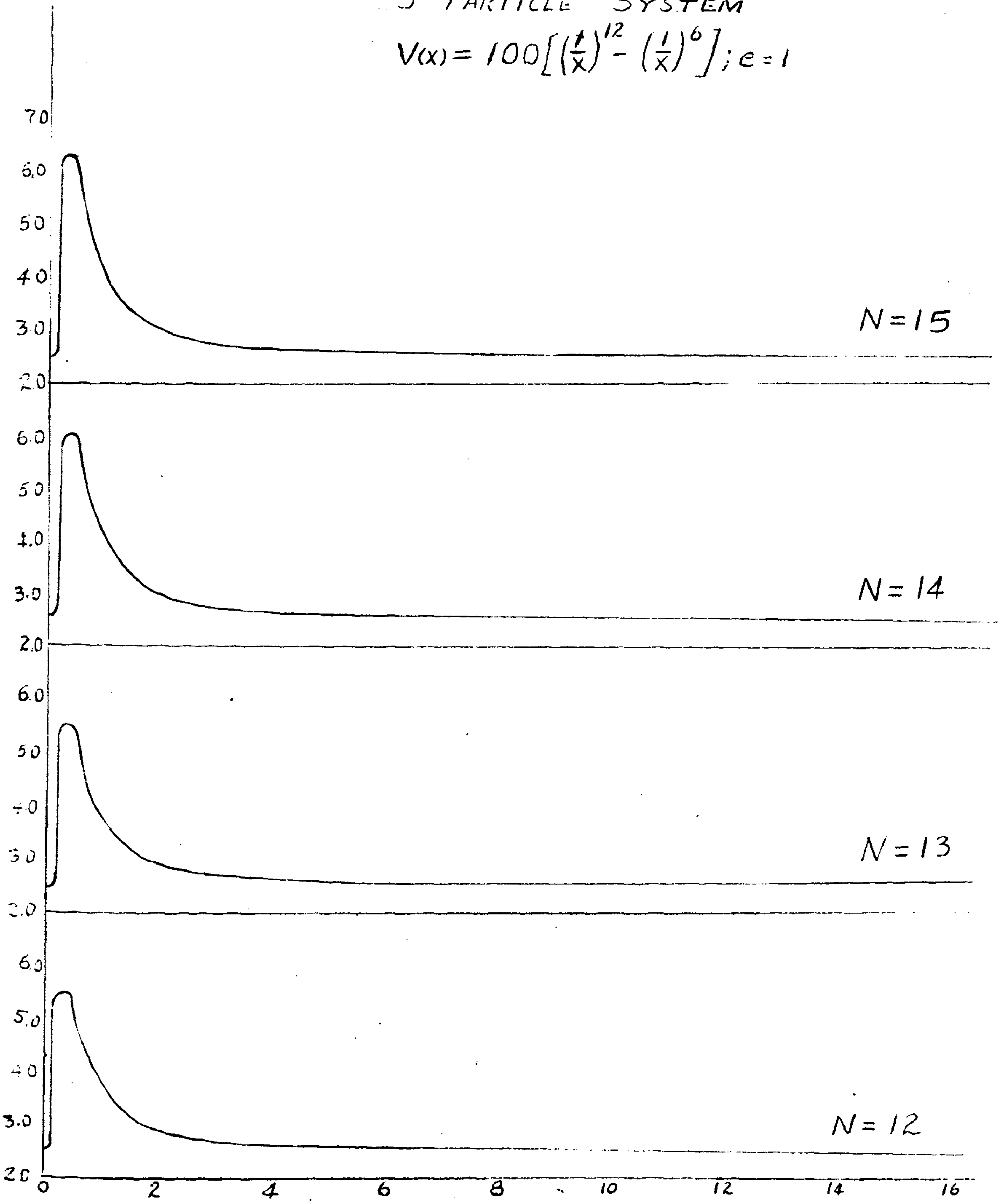


FIG. 30

Correlation Function vs Separation

5 Particle System

$V(x) = -64\left(\frac{2}{x}\right)^6$; $e=2$, $T=5°$

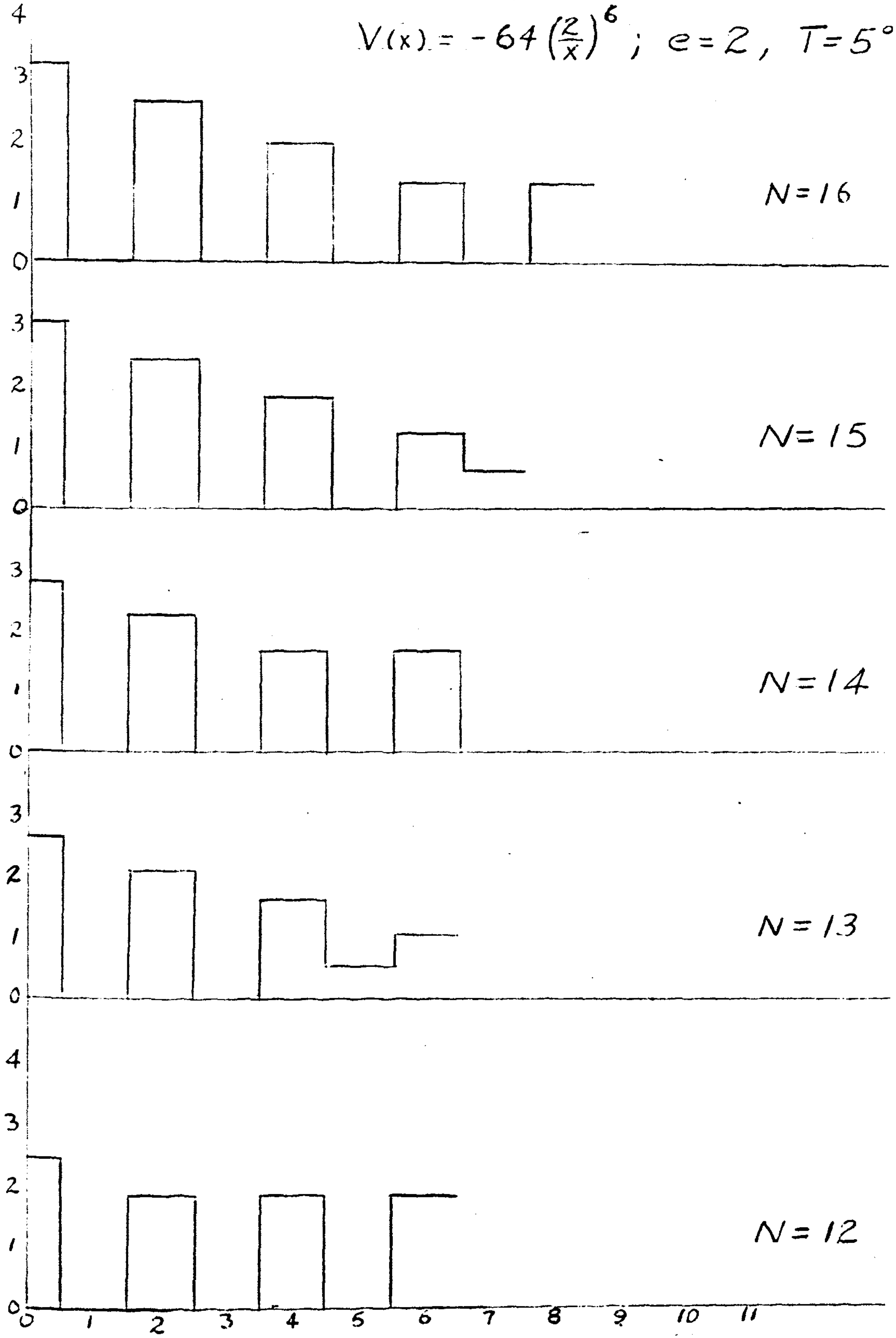


Fig. 31

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = -64\left(\frac{2}{x}\right)^6; \quad e=2, \; T=5^\circ$

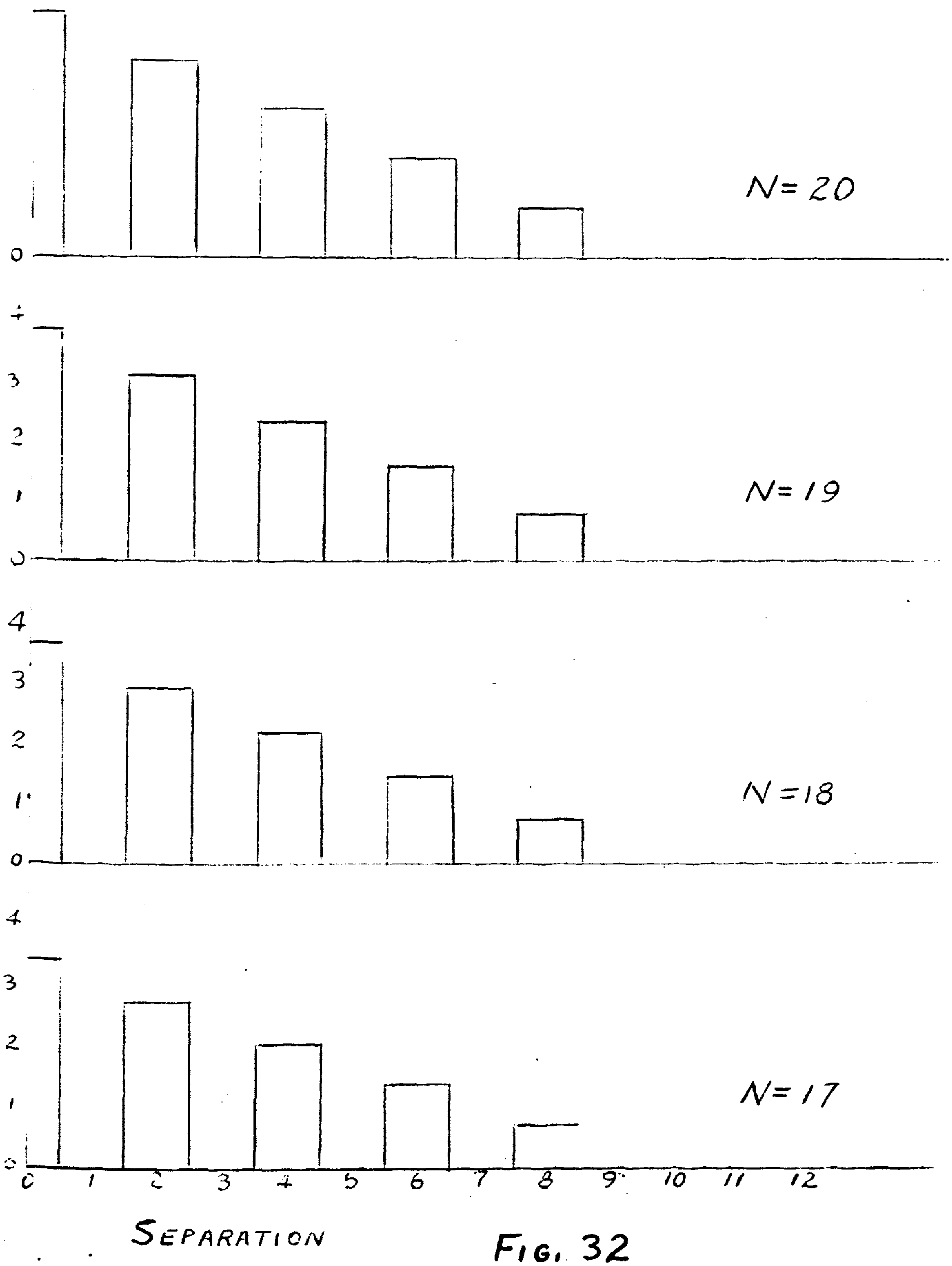


FIG. 32

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = -64\left(\frac{2}{x}\right)^6, e=2, T=5°$

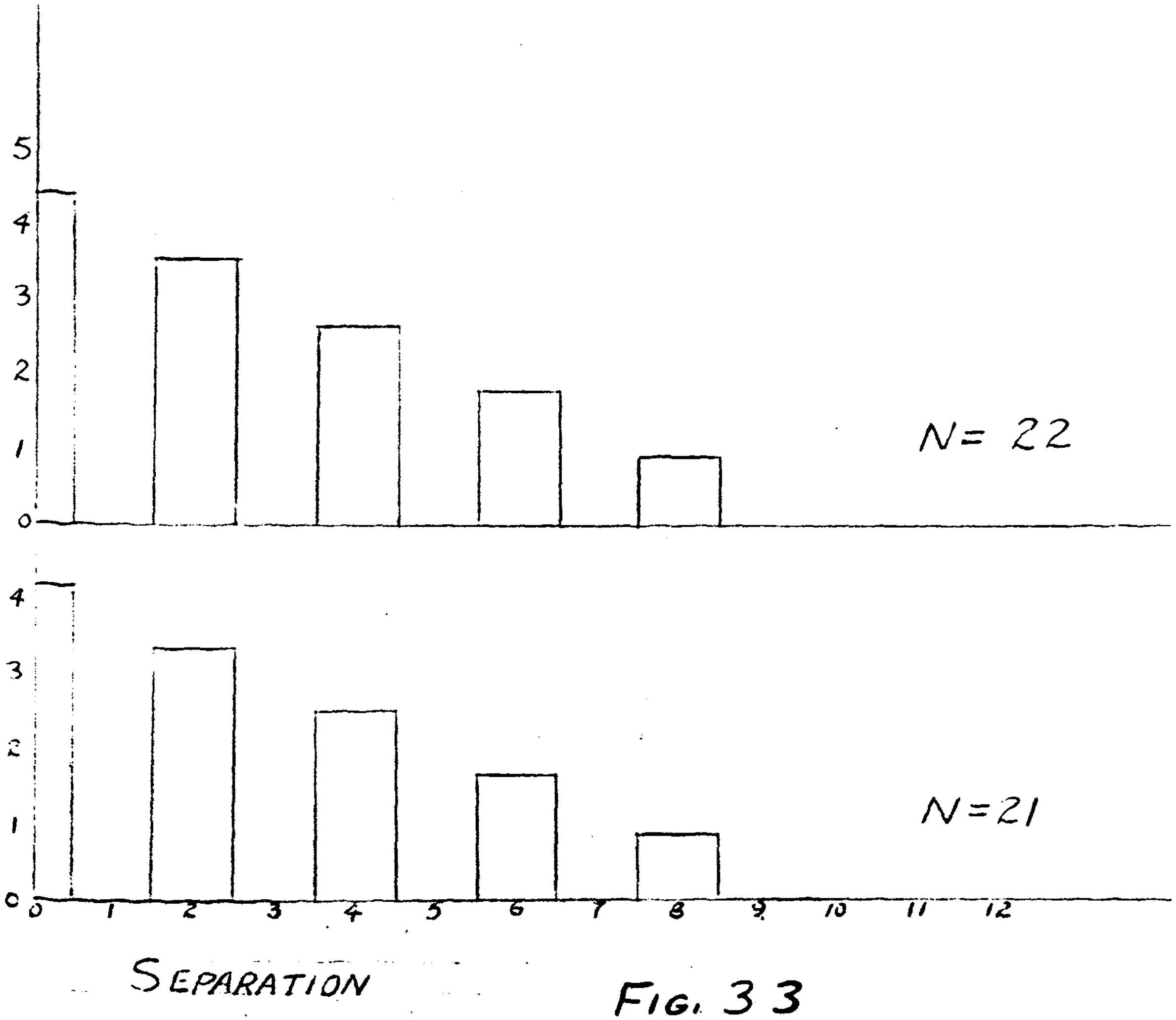


FIG. 33

PRESSURE VS VOLUME

5 PARTICLE SYSTEM

$V(x) = -64\left(\frac{2}{x}\right)^6$; $e=2$, $T=5°$

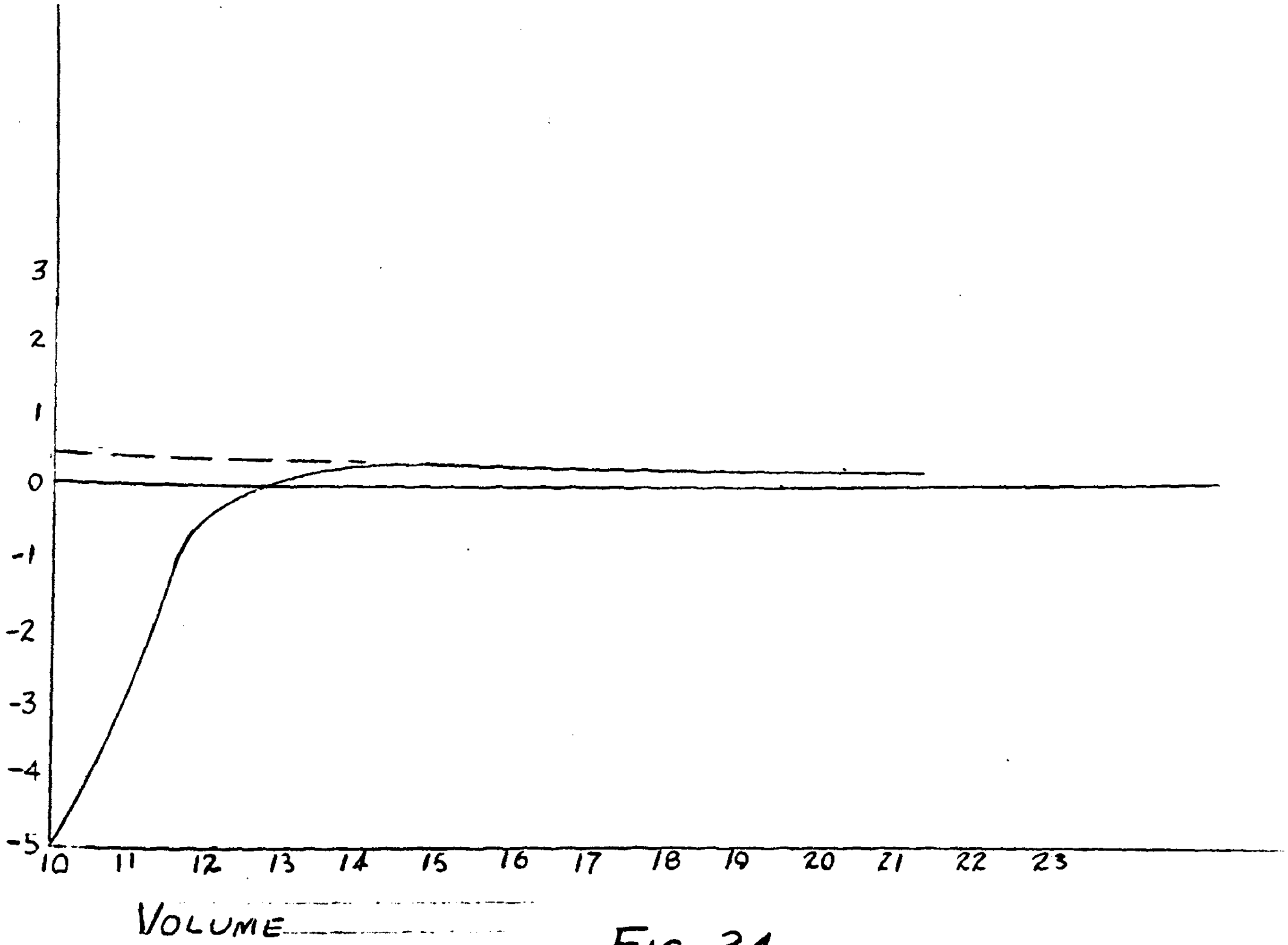


FIG. 34

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = 0 \; ; \; e = 2$

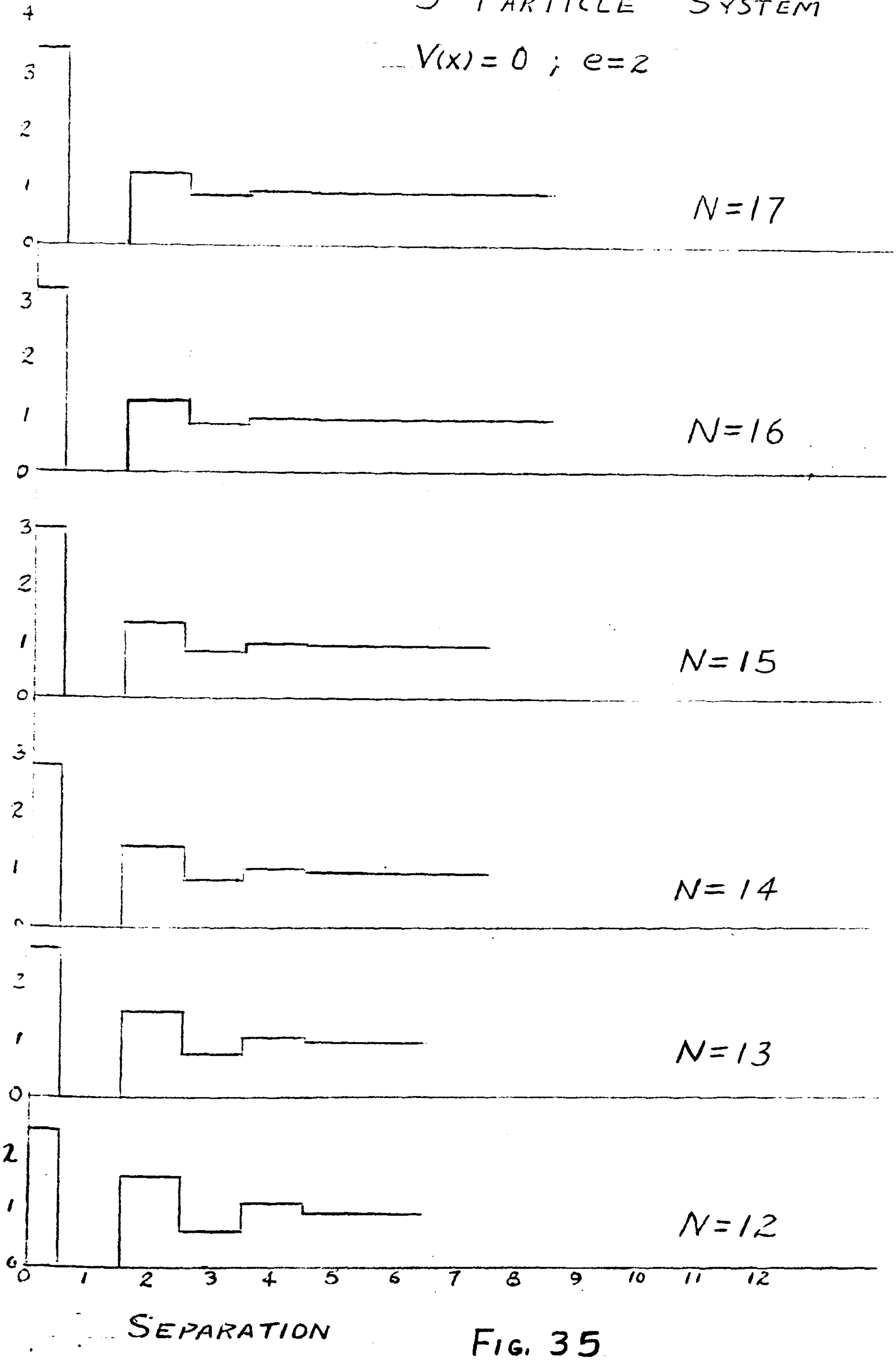


FIG. 35

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = 0 \,;\ e = 2$

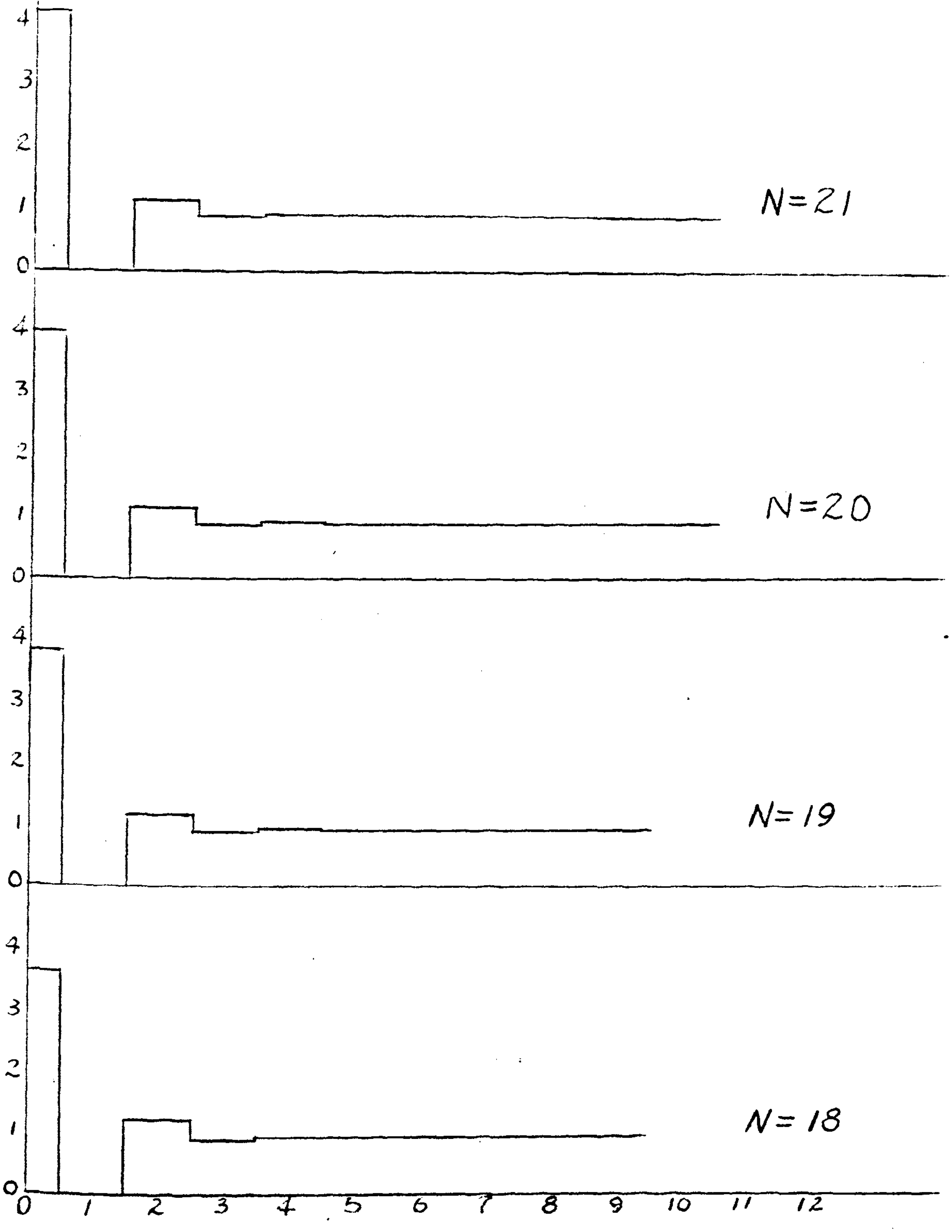


FIG. 36

CORRELATION FUNCTION VS SEPARATION

5 PARTICLE SYSTEM

$V(x) = 0, \ \epsilon = 2$

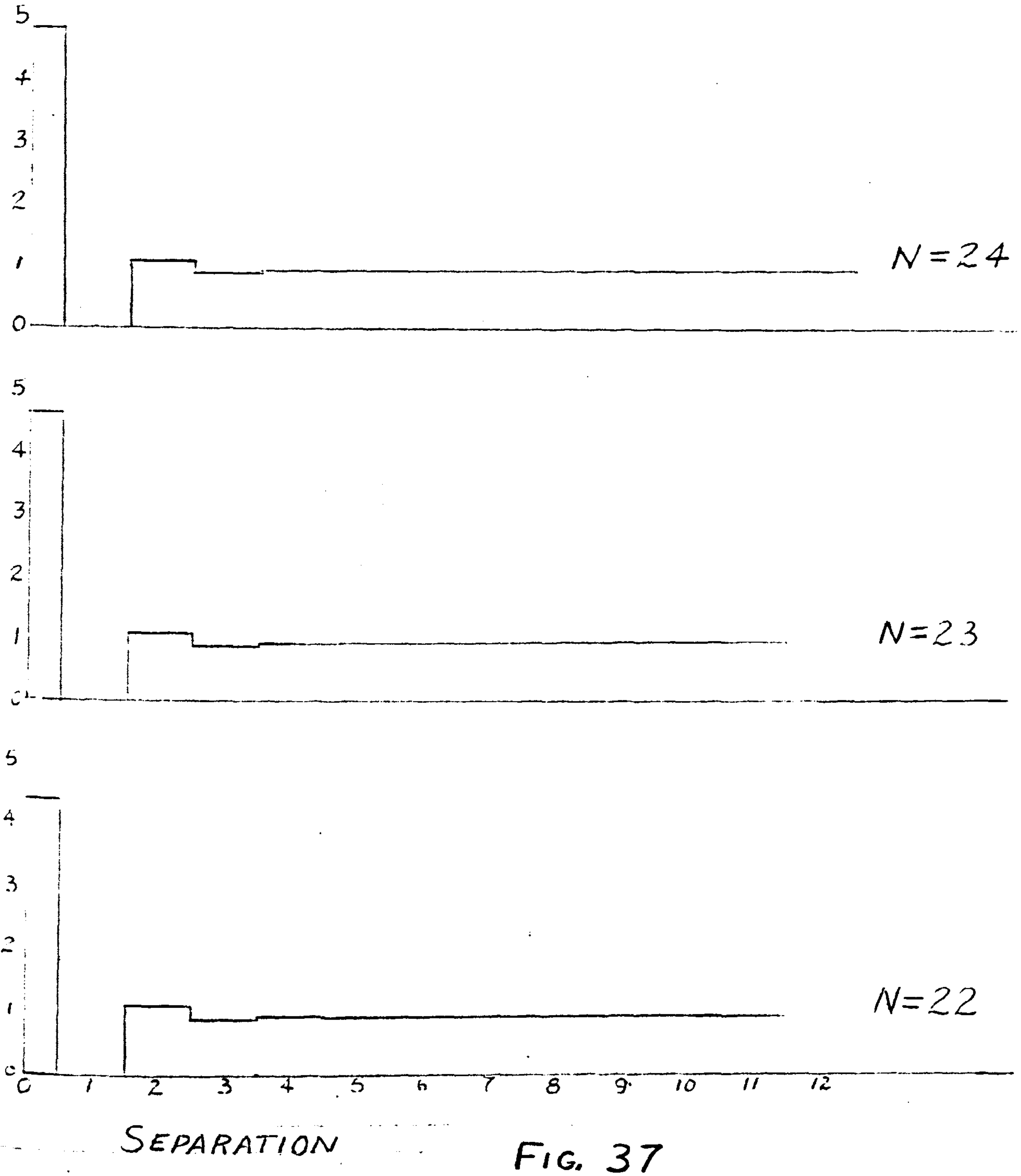


FIG. 37

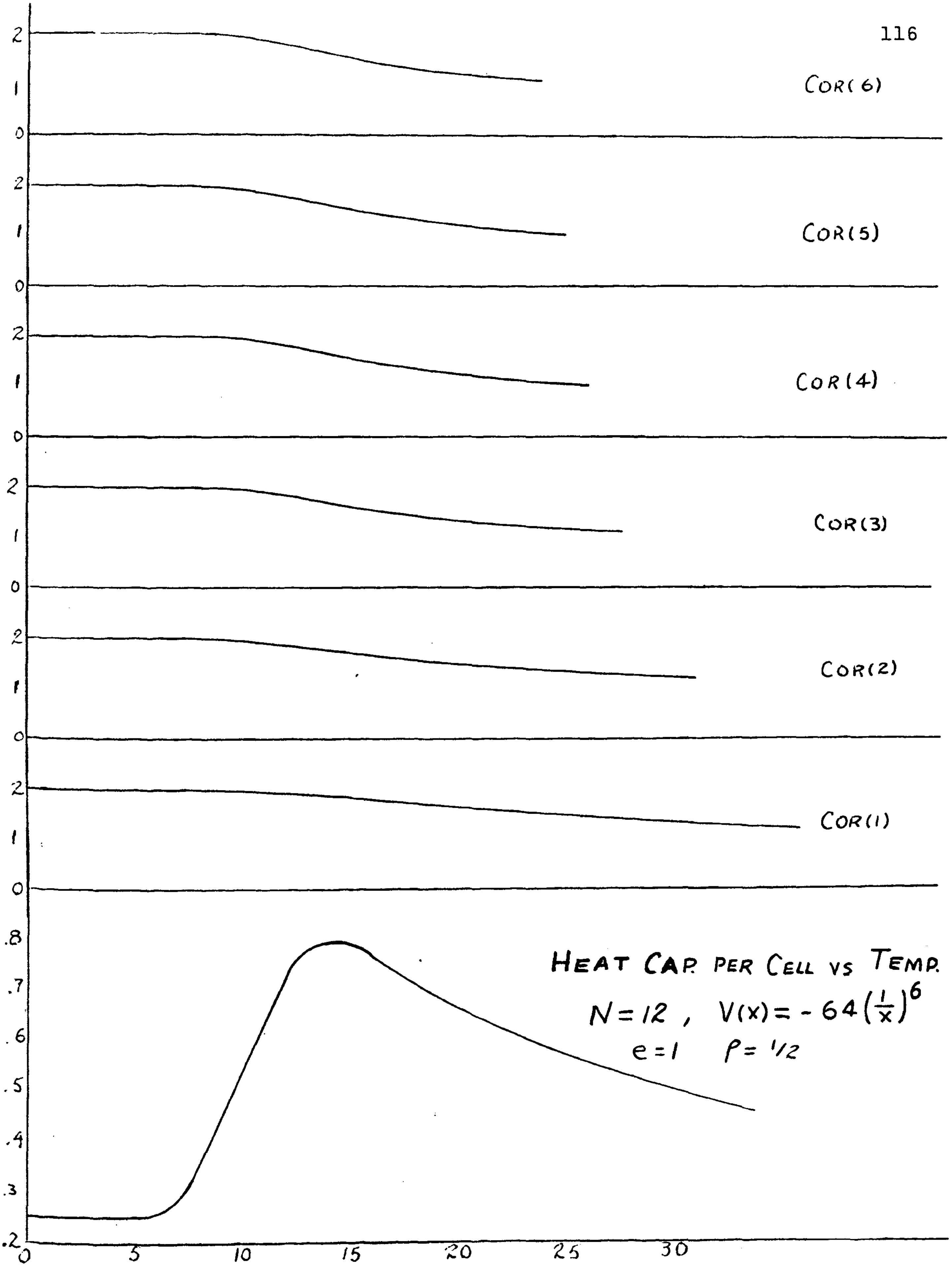
way the system behaves. There are peaks at 2, 4, 6, etc. The ideal volume of this sytem is one in which every other cell is occupied. Since n = 5 this would be a 10 celled system. Figures 32 and 33 reveal more plots. Notice that the plots for N = 17, 18, 19, 20, 21, and 22 are all exactly alike differing only in height. This indicates that the controlling configuration is stable enough to be unaffected by increased volume. On the basis of our earlier results, we would expect the system to tend to its most preferred configuration, namely the close-packed N = 10 volume. Hence we should expect negative values of pressure in the neighborhood of N = 10. This is indeed the case as Figure 34 shows.

Finally, one would like to know how the correlation function for a completely random system would appear. Figures 35, 36 and 37 show the correlating function for a non-interacting system of particles with a hard core diameter of 2 cells. Note that the curves are not completely flat but reveal the local fluctuations one expects to find in such plots. Since e = 2 cor(1) = 0. Then cor(2) will be max. because there is more system available than in the other cases. However, cor(3) < cor(4) because having a pair of particles 3 cells apart blocks out 5 cells from occupancy because there is only 1 empty cell between them. A pair of particles 4 cells apart only block out 4 cells since there are two free cells in between so that a third particle can just fit. There would be more configurations for a separation of 4 than for a separation of 3. In Tross' work no such local maxima were observed. This was because he assumed e = 1. Thus allowing only separations of an integral number of particle diameters, hence eliminating separations which are not the most favorable.

From a study of Figures 35, 36, and 37 it is clear that the behavior we have seen previously is totally different, that the correlation is not that of a random system but of an ordered one.

B. Grand Canonical Ensemble

We now proceed to examine the computer results for the grand ensemble calculations. Again we allow for the most widely variant situations we can. We can vary the number of cells, the particle diameter, the potential, and the temperature arbitrarily. Only time limitations prevent us from examining systems of arbitrarily large size. We start these presentations with a set of curves for a 12 celled system with the interaction $v(x) = -64/x^6$ with e = 1. These calculations were made by Tross and presented in his papers in the Journal of Mathematical Physics.[5] See Figures 15 and 18 of that work. These compare with Figures 38 and 39 respectively. It is heartening to note that they are identical except that he has plotted $\beta P \ell$ instead of P against the density. We have set $\ell = 1$ and $k = 1$ in this study and hence $\beta = 1/T$ so that the values of



HEAT CAP. PER CELL VS TEMP.

$N = 12$, $V(x) = -64\left(\frac{1}{x}\right)^6$

$e = 1$ $\rho = 1/2$

FIG. 38

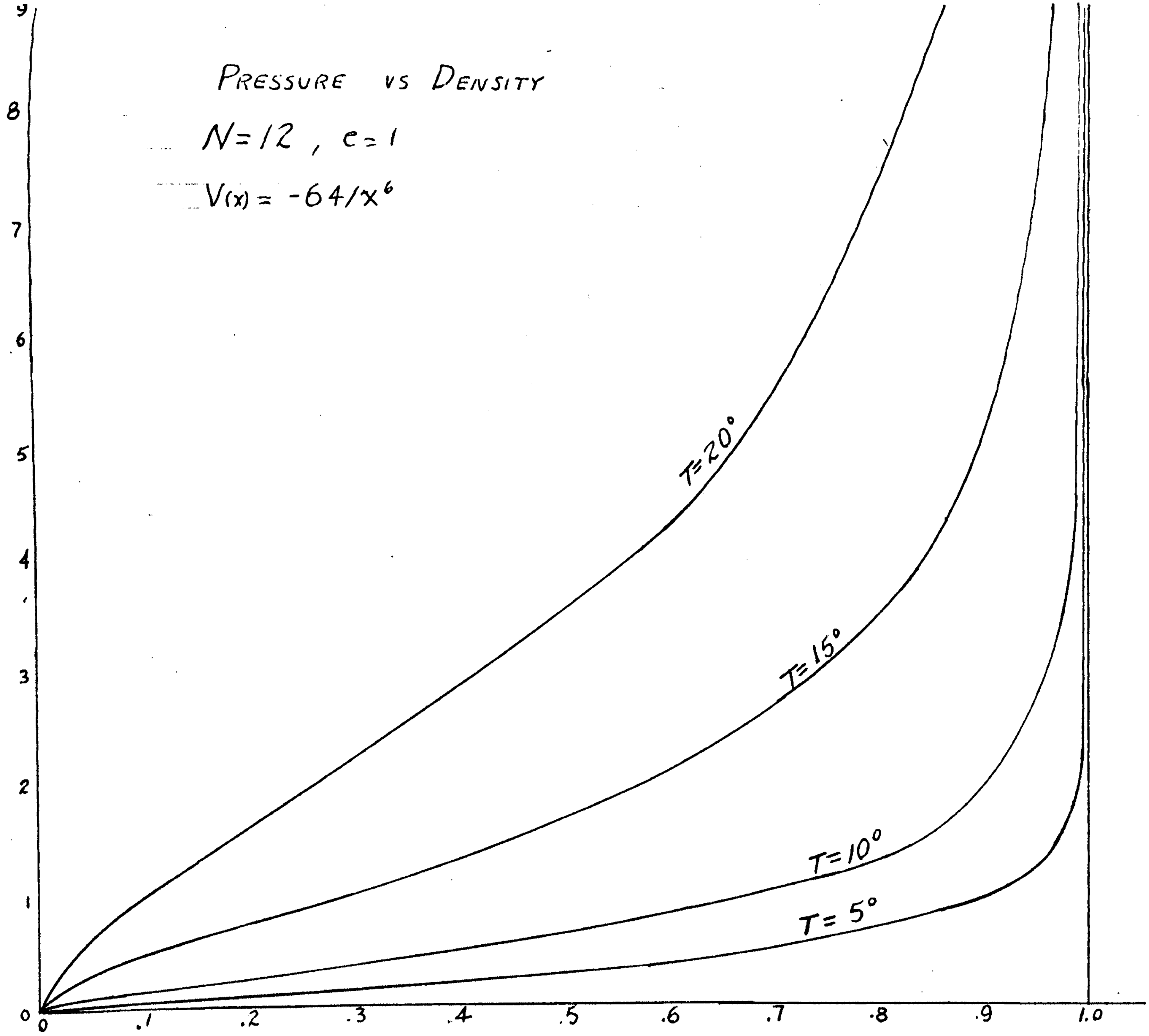

PRESSURE vs DENSITY
N=12 , e=1
V(x) = -64/x^6
T=20°
T=15°
T=10°
T= 5°
0
1
2
3
4
5
6
7
8
9
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
DENSITY

FIG. 39

P in Figure 38 should be divided by the temperature to compare with Figure 18 of the paper. The agreement between these two calculations performed in somewhat different ways reinforces ones trust that both methods are valid. Of course, as we have shown, the two methods are closely related. Figure 38 contains a plot of the heat capacity per cell versus the temperature. We have divided the heat capacity by the number of cells for comparison purposes and we shall continue this in the grand ensemble calculations. The comparison of this curve with the curve in the above-mentioned paper for $\zeta = 64k$ reveals the identity of the results. Figure 38 also contains plots of the various components of the correlation against the temperature. Notice that the heat capacity per cell is largest when the various components are changing most rapidly.

Next we look at results obtained using a potential interaction $V(x) = -32\delta(x - 2)$ with a hard core diameter $e = 1$. Figure 40 shows a plot of heat capacity per cell versus temperature. Note the peak and that it occurs in the same interval where the correlation values also plotted in Figure 40 are changing most rapidly. Figure 41 shows the pressure plotted as a function of density for the same system for several temperatures. No unusual behavior is observed here.

Figure 42 shows a plot of the heat capacity per cell and plots of the correlation function for a system of

CORRELATION & HEAT CAP. PER CELL VS TEMP. $N = 12$, $\rho = 1/2$

$V(x) = -32\,\delta(x-2)$; $e = 1$

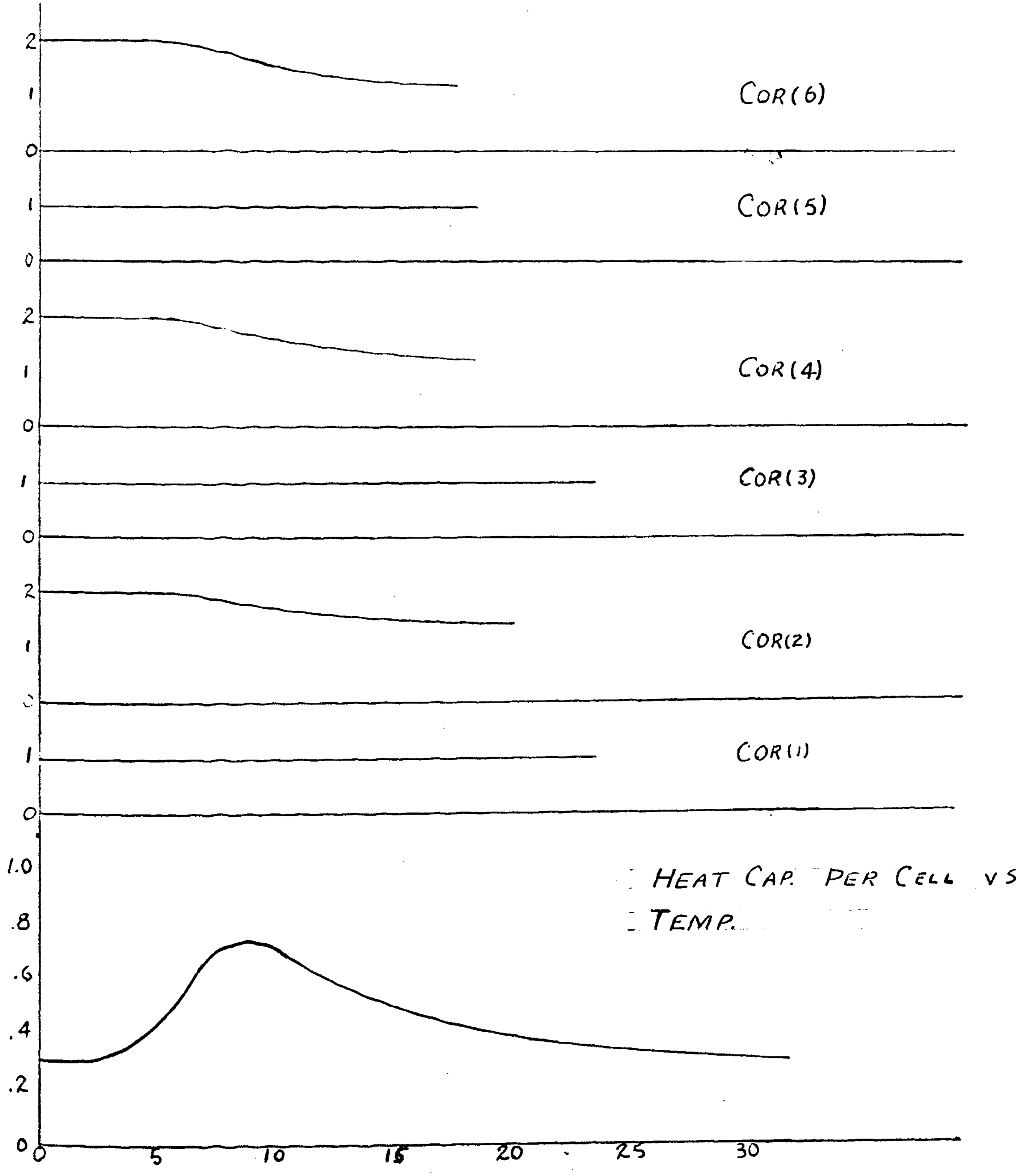


FIG. 40

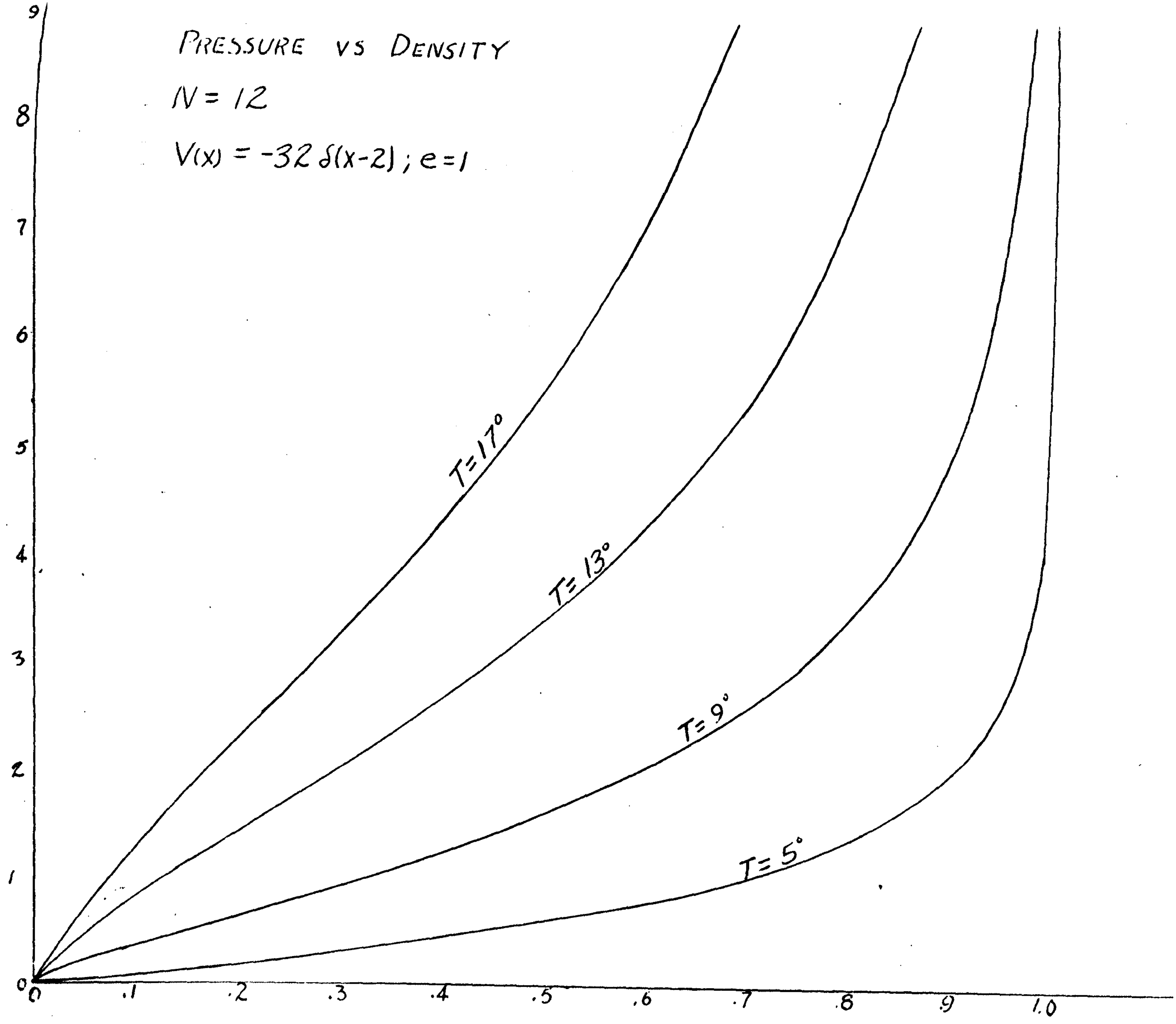

Pressure vs Density
N = 12
V(x) = −32 δ(x−2) ; e = 1
T = 17°
T = 13°
T = 9°
T = 5°
0
1
2
3
4
5
6
7
8
9
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
Density

Fig. 41

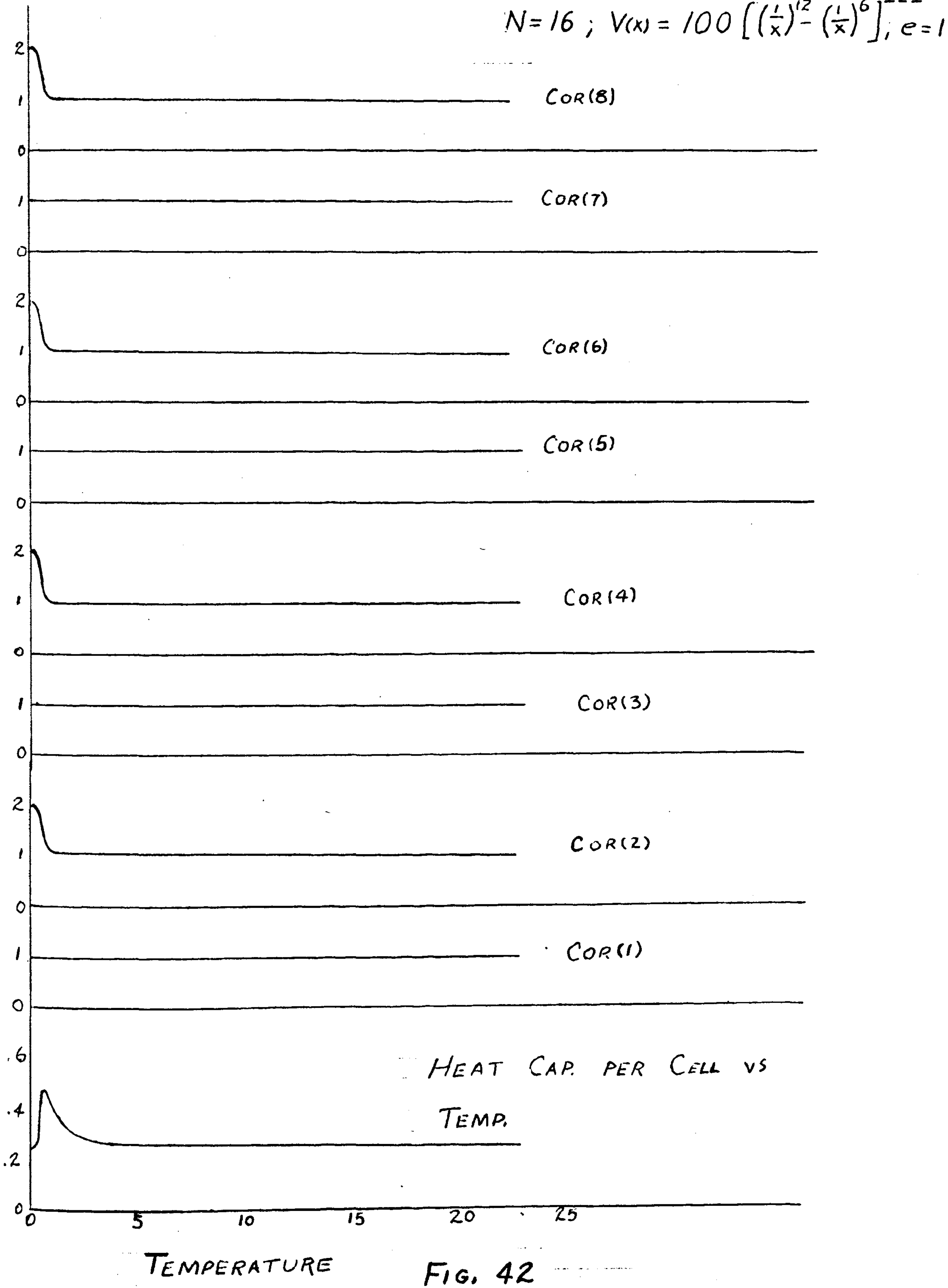

$N=16$; $V(x) = 100\left[\left(\frac{1}{x}\right)^{12} - \left(\frac{1}{x}\right)^{6}\right]$, $e=1$
COR(8)
COR(7)
COR(6)
COR(5)
COR(4)
COR(3)
COR(2)
COR(1)
HEAT CAP. PER CELL VS TEMP.
2
1
0
.6
.4
.2
0
5
10
15
20
25
TEMPERATURE

FIG. 42

16 cells, the largest volume considered for e = 1. The interaction potential used for this calculation was $V(x) = 100[x^{-12} - x^{-6}]$. As was the case for the canonical system which employed this potential, the heat capacity curve peaks below 1° and reduces to its ideal gas limit rather quickly thereafter. Note the behavior of the correlation function both here and in the previous case. For even separations, it starts at the maximum value 2 and relaxes quickly to 1 while at odd values of the separation the correlation value starts and stays at 1. This similarity may suggest that other similarities exist between the two systems. Figure 43 reveals nothing in the way of unusual behavior of the pressure as the density changes.

We next examine the results of the grand canonical calculations for several systems for the potential $V(x) = 100[(\frac{2}{x})^{12} - (\frac{2}{x})^{6}]$ which produced such unusual results in the canonical ensemble. To prevent problems on the computer we redefine V(1) so that V(1) = 10 a number which is more manageable on the machine. We first take e = 1. We recall the unusual behavior of the system around a density of 1/3. Figure 44 is a plot of correlation function versus separation for various densities in both ensembles. For $\rho = 1/4$ the canonical ensemble results differ from the grand ensemble in that the values from the former are less than the corresponding ones of the grand ensemble.

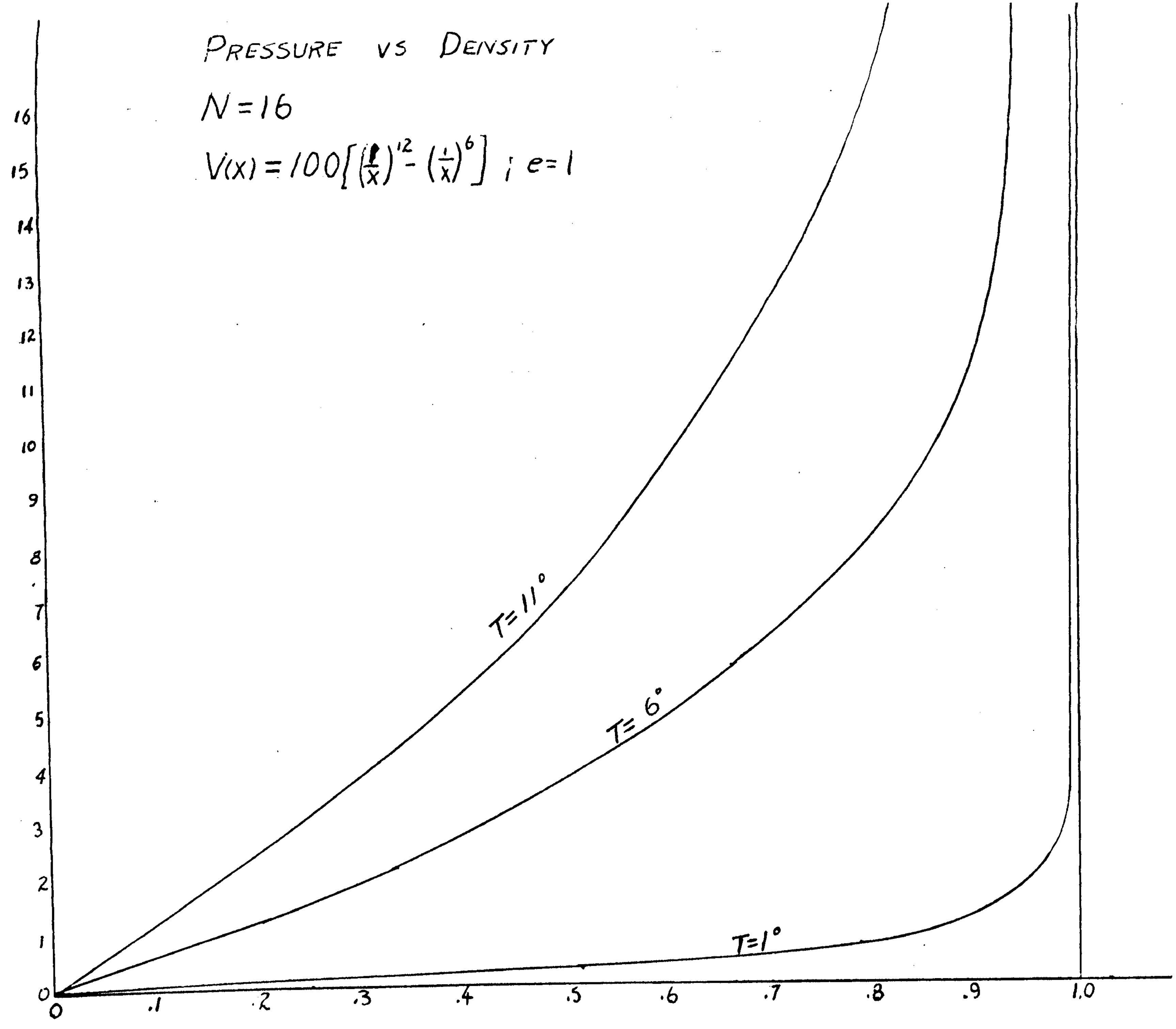

PRESSURE VS DENSITY
N=16
$V(x)=100\left[\left(\frac{1}{x}\right)^{12}-\left(\frac{1}{x}\right)^{6}\right]$; e=1
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
T=11°
T=6°
T=1°
DENSITY

FIG. 43

CORRELATION FUNCTION VS SEPARATION

$N = 12$, $T = 1°$

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $e = 1$

$V(1) = 10$

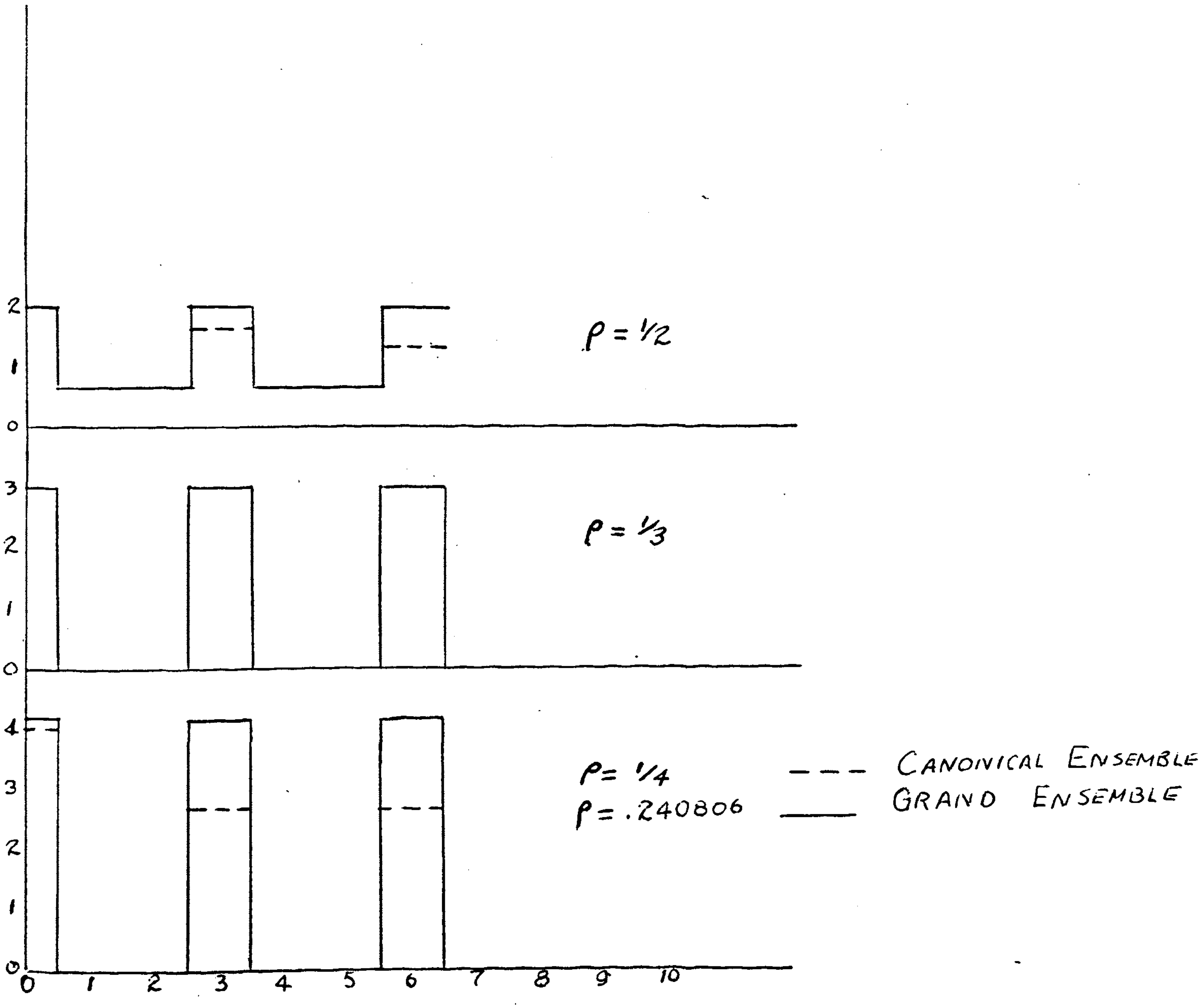


FIG. 44

For $\rho = 1/3$ both ensembles yield the same results showing as before perfect correlation at separations of 3 cells, 6 cells. At $\phi = 1/2$ the two ensembles again differ with the successive peaks of the canonical ensemble decreasing in height while the grand ensemble peaks are all of equal height. These results were obtained at a temperature of 1 degree. Figure 45 records the results of heat capacity per cell versus temperature for the grand ensemble and correlation function against temperature for both ensembles. The behavior of correlation functions in both ensembles is seen to be quite similar though not identical.

Figure 46 shows the correlation function versus temperature for both ensembles again note the similar behavior. Now we come to the most startling curve of all. Figure 47 shows the pressure plotted against density for several values of the temperature. Note the unusual behavior of the $T = 1^\circ$ curve in the neighborhood of $\rho = 1/3$ and $\rho = 2/3$ the nearly vertical portions of the P-ρ curve followed by the nearly horizontal portions. This behavior persists through higher temperatures but seems to disappear around $T = 6^\circ$. After $T = 6^\circ$ the curves show no unusual behavior. We now look at a 15 cell system. We first see plots of the canonical correlation function versus separation in Figure 48 for the various numbers of particles from $n = 2$ to $n = 7$. For $n = 2$ we see only the peak at 3 cell separation. For $n = 3$ we note a new peak at 6 which is just 1/2 as high as

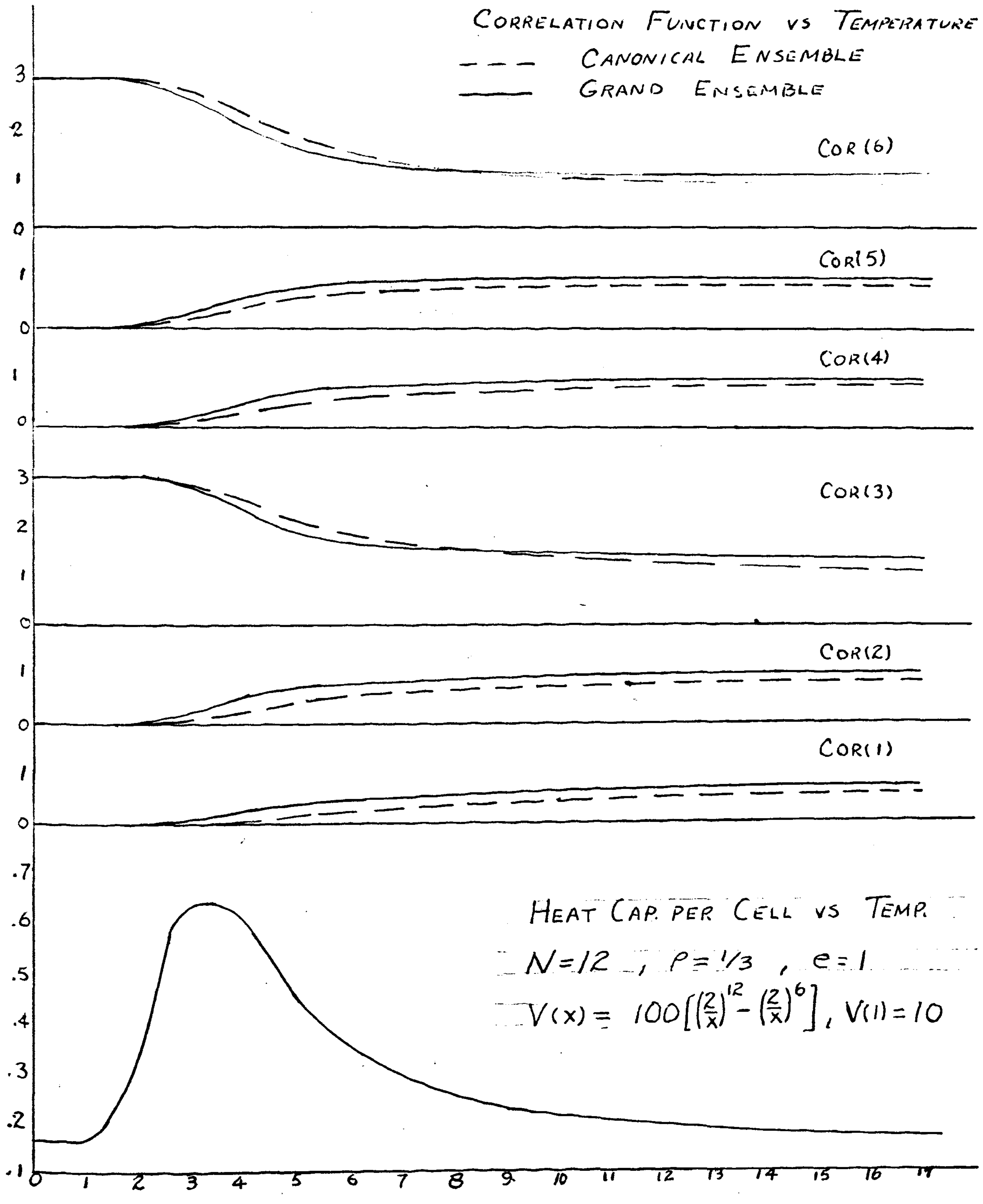
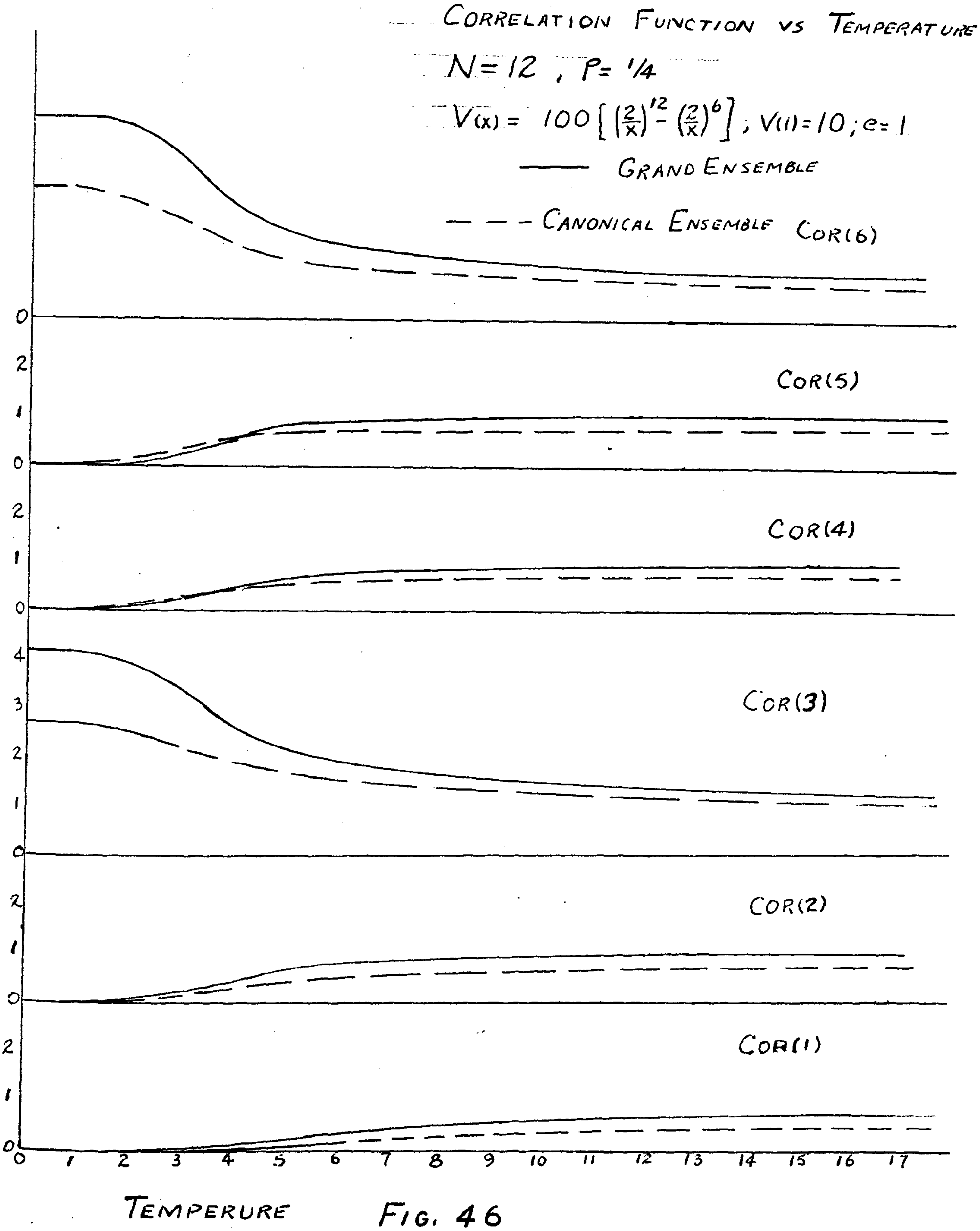

CORRELATION FUNCTION VS TEMPERATURE
- - - CANONICAL ENSEMBLE
—— GRAND ENSEMBLE
COR (6)
COR(5)
COR(4)
COR(3)
COR(2)
COR(1)
3
2
1
0
1
0
1
0
3
2
1
0
1
0
1
0
.7
.6
.5
.4
.3
.2
.1
HEAT CAP. PER CELL VS TEMP.
N=12 , ρ=1/3 , e=1
$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$, V(1)=10
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
TEMPERATURE

FIG. 45



CORRELATION FUNCTION VS TEMPERATURE

$N=12$, $\rho = 1/4$

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $V(1)=10$; $e=1$

FIG. 46

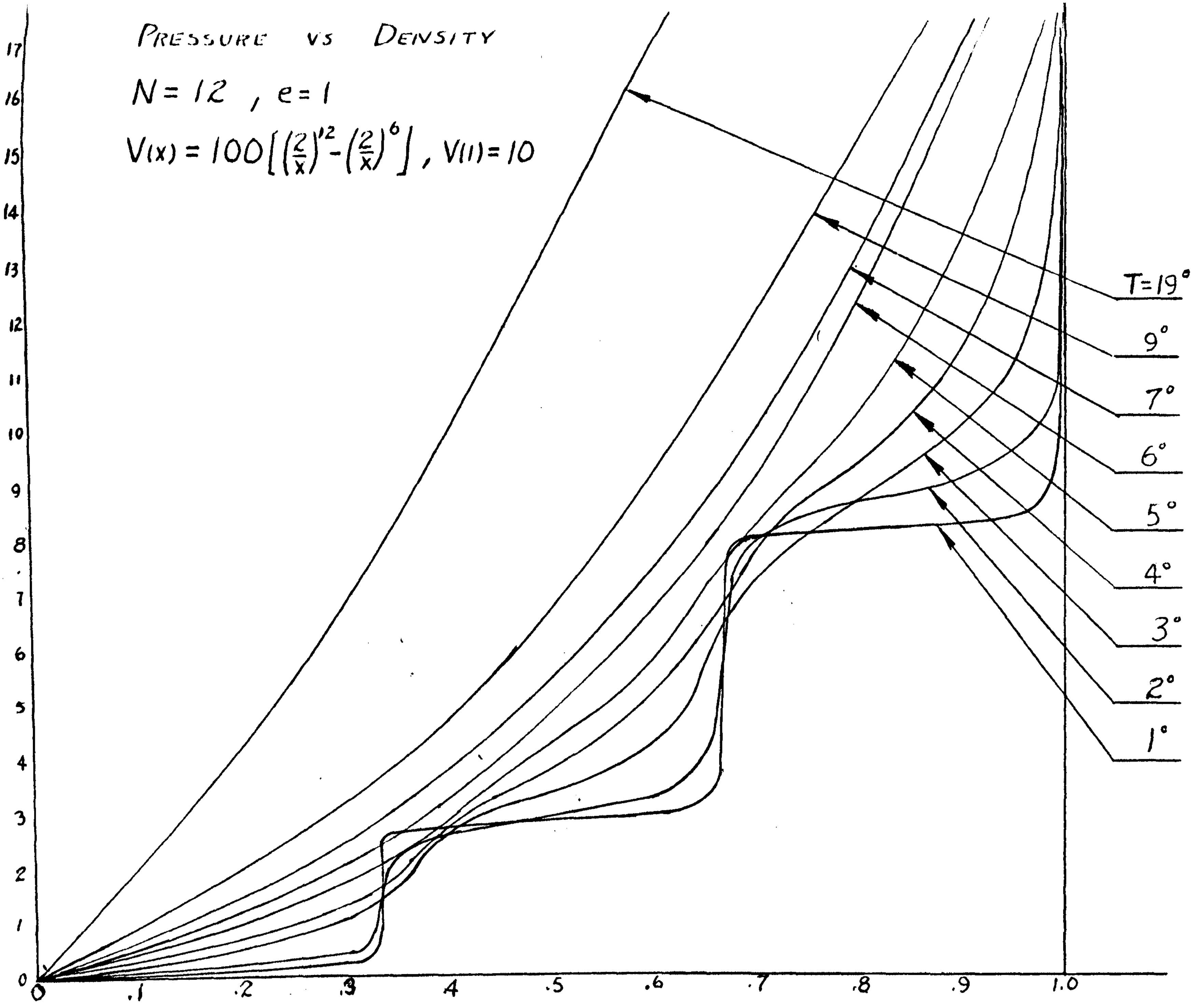

PRESSURE VS DENSITY
$N = 12$, $e = 1$
$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$, $V(1) = 10$
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
T=19°
9°
7°
6°
5°
4°
3°
2°
1°
DENSITY

FIG. 47

CORRELATION FUNCTION VS SEPARATION

15 CELLS , $T = 1°$, $e = 1$

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$; $V(1) = 10$

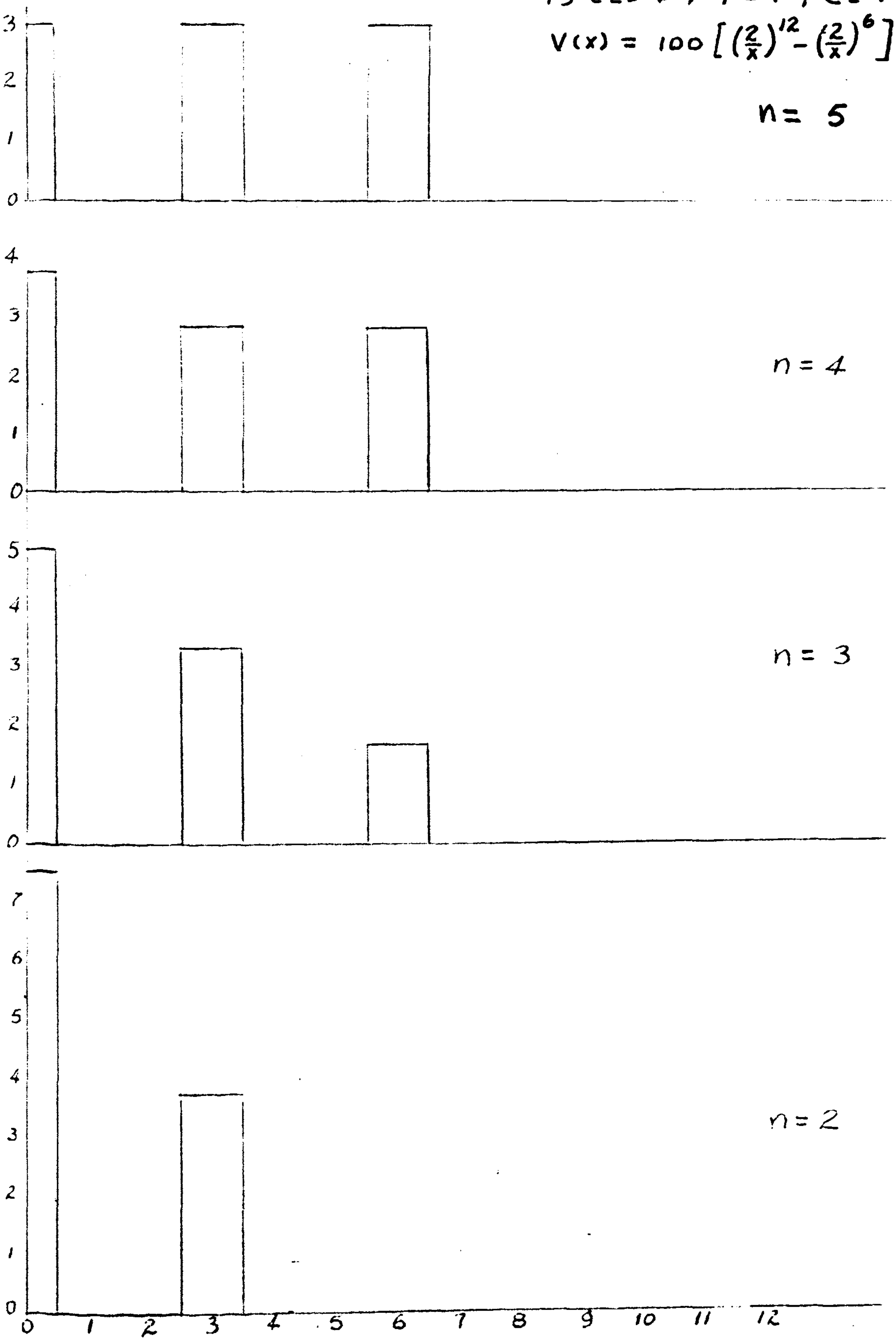


FIG. 48

the one at 3 and 1/3 the height of the self-correlation peak. At n = 4 the peak at 6 has grown to the same height as the peak at 3 but not to the height of the self-correlation peak. At n = 5 the magical density $\rho = 1/3$ all peaks are of equal height. Figure 49 has the plots for n = 6 and n = 7. Notice the growing background correlation since the system now has more particles than it can comfortably hold.

Figure 50 shows plots of the various values of the grand canonical correlation function against temperature at the magical 1/3 density. Note that at low temperature peaks occur at 3 and 6 with zero or small values in between. As the temperature increases, note that all values of the correlation function approach 1. Figure 51 plots the pressure against the density and as in the case N = 12 the T = 1° curve is most unusual. Again the anomalous behavior occurs in the neighborhood $\rho = 1/3$ and $\rho = 2/3$. Note that by the time T = 6° this anomalous behavior disappears. The values of the pressure for a given density for both systems (consider N= 12 and N = 15) agree to within a few per cent showing how slowly the pressure changes with volume as the density is held fixed. Figure 52 considers the same potential but for a system where e = 2 and N = 18 plotting the heat capacity per cell versus temperature for $\rho = 1/3$. Note that as before the major departure of the heat capacity per cell from the ideal gas value occurs around T = 2° and returns near

CORRELATION FUNCTION VS SEPARATION

15 CELLS

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$, $V(1)=10$, $e=1$, $T=1°$

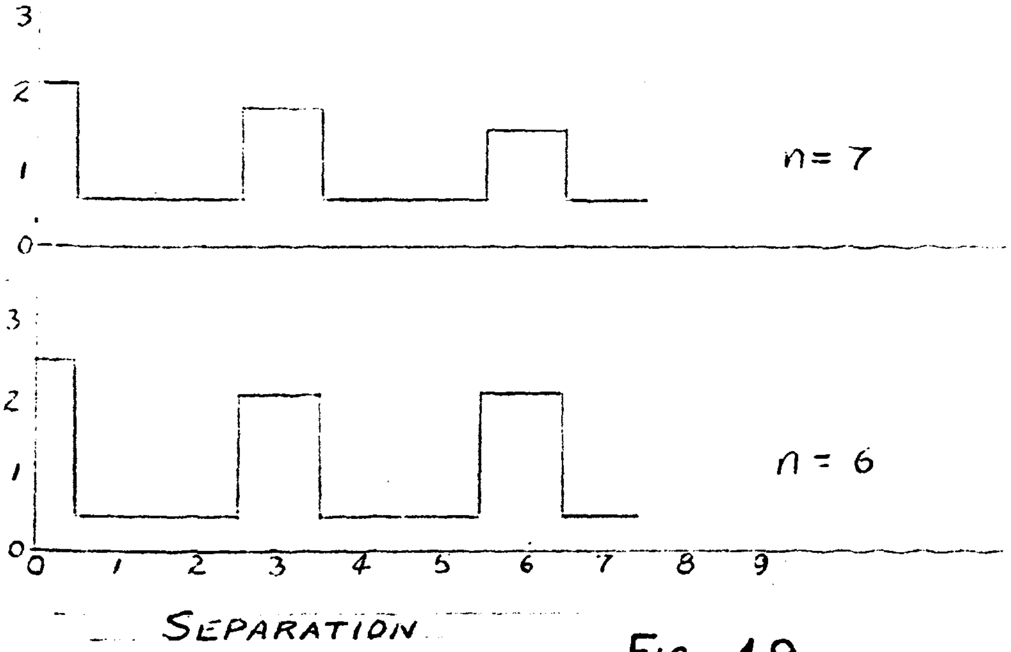


FIG. 49

CORRELATION FUNCTION VS TEMPERATURE $N=15$ $\rho=1/3$

GRAND CANONICAL ENSEMBLE

$$V(X) = 100\left[\left(\frac{2}{X}\right)^{12} - \left(\frac{2}{X}\right)^{6}\right];\ e=1$$

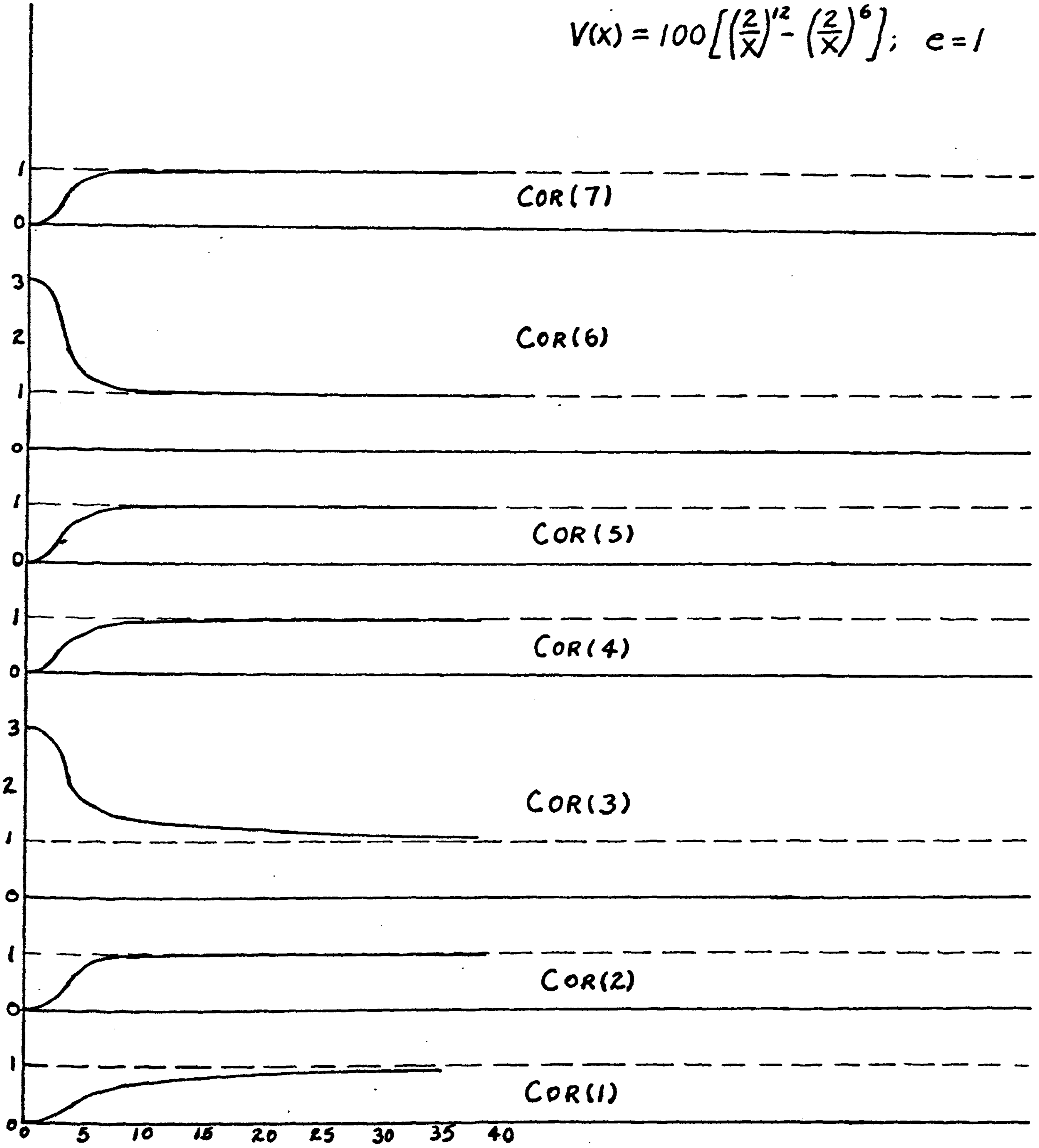


FIG. 50

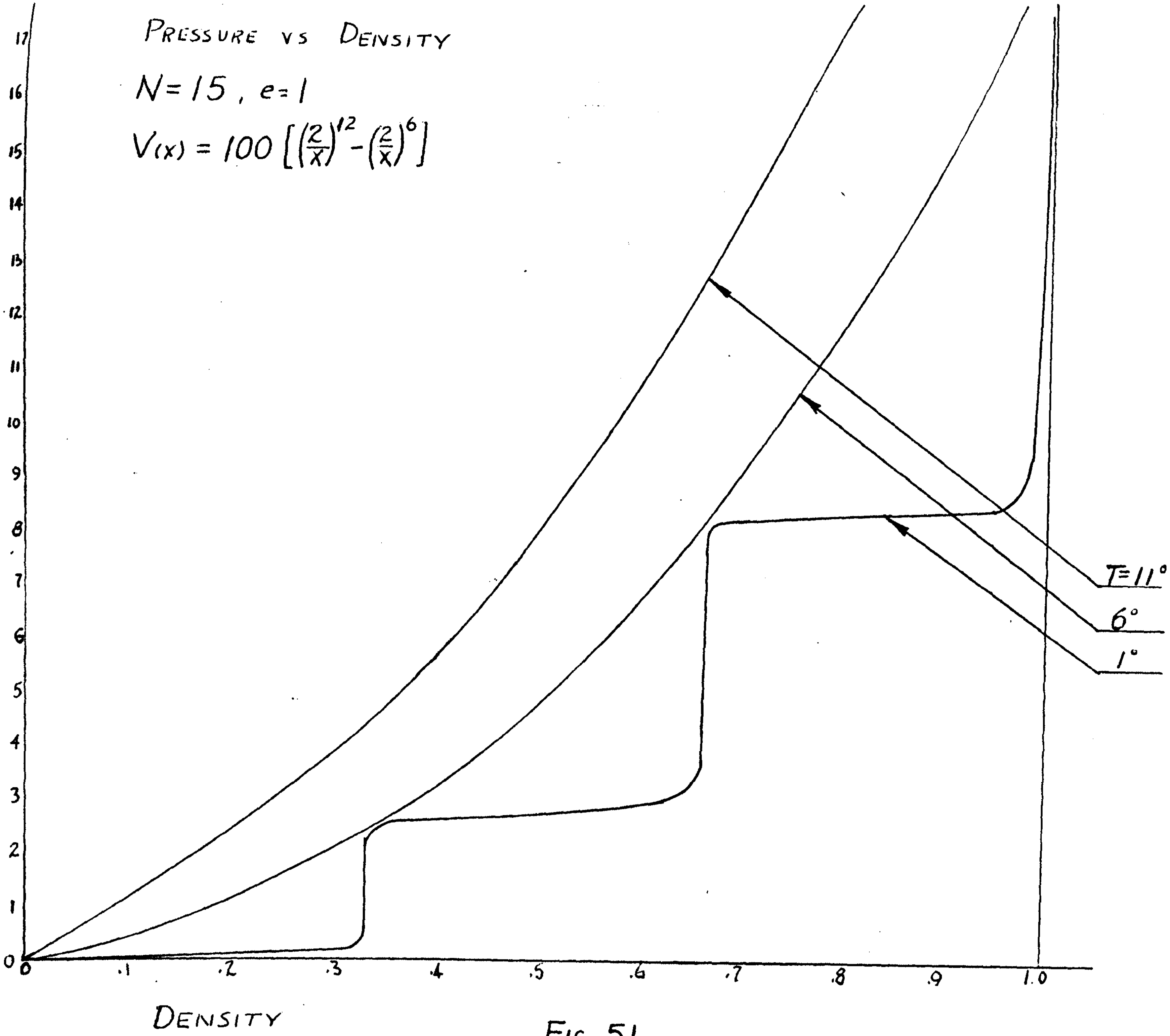

PRESSURE VS DENSITY
N=15, e=1
V(x) = 100 [(2/X)^12 - (2/X)^6]
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
T=11°
6°
1°
DENSITY

FIG. 51

HEAT CAP. PER CELL VS TEMP.

$N = 18$, $\rho = 1/3$, $e = 2$

$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$

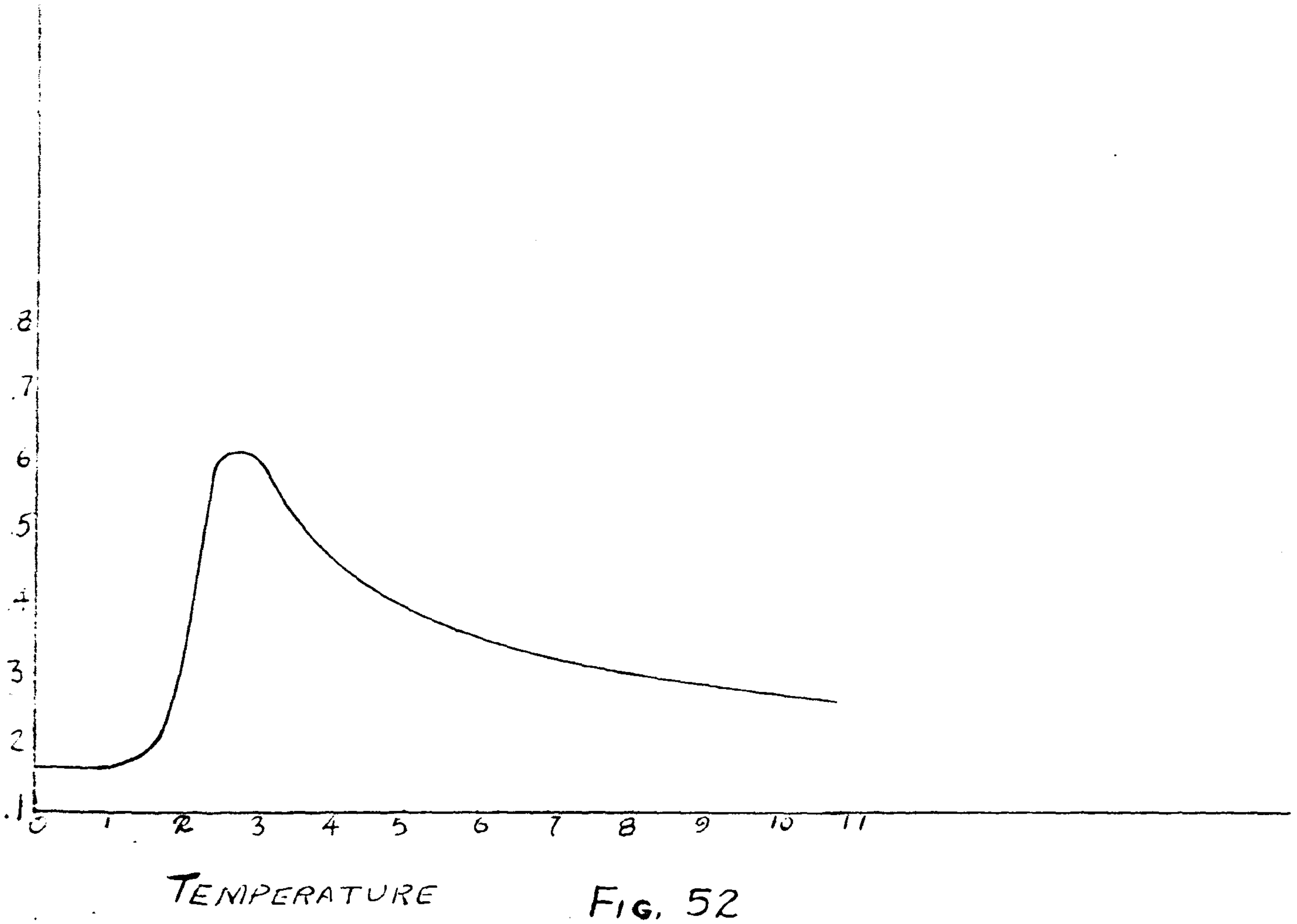


FIG. 52

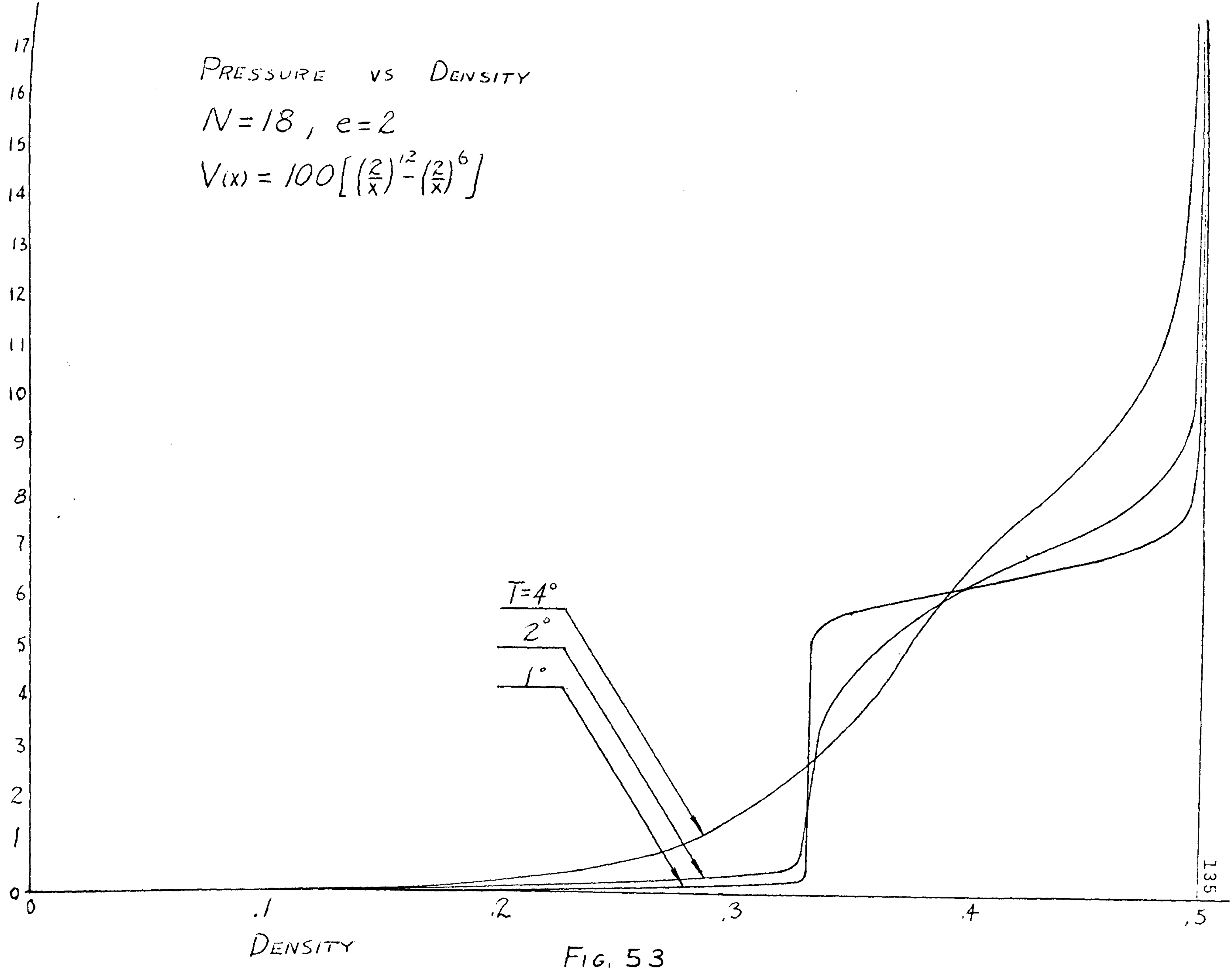

PRESSURE VS DENSITY
$N = 18$, $e = 2$
$V(x) = 100\left[\left(\frac{2}{x}\right)^{12} - \left(\frac{2}{x}\right)^{6}\right]$
T=4°
2°
1°
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
.1
.2
.3
.4
.5
DENSITY

FIG. 53

$T = 10°$. Since $e = 2$ the density cannot exceed 1/2 so that the vertical portion formerly observed at $\rho = 2/3$ in the other cases for the P-ρ curves at $T = 1°$ cannot occur here. Figure 53 shows the behavior of P with changing density for $T = 1°$, $2°$, and $4°$. We continue to observe the anomalous behavior about $\rho = 1/3$ as in the cases where $e = 1$. As expected, this behavior begins to disappear as the temperature increases.

We have seen how the computer data turned out that many unexpected results turned up, let us now attempt to explain these results.

CHAPTER V

ANALYSIS OF COMPUTER RESULTS

The results obtained in the calculations are quite surprising at first meeting. The peculiar behavior of the pressure-volume curves in the canonical ensemble or pressure-density curves from the grand ensemble treatment is one of the things for which an explanation is required.

The number of configurations in the lattice partition functions is finite for any finite number of lattice points or cells. This means that there are a finite number of energy levels. Thus we can order these levels starting from the lowest state to the highest. Suppose there are m different energy levels for a particular system. We label these in increasing order so that

$$u_1 < u_2 < u_3 < \cdots < u_m \tag{146}$$

Suppose that the multiplicity of the level u_1 is g_1, that of u_2 is g_2, etc. Then we have

$$C_n(N,\beta) = \sum_{i=1}^{m} g_i e^{-\beta u_i} \tag{147}$$

The quantities g_i depend only on the geometry and boundary conditions of the system and do not depend on the temperature. This means that all the temperature variation of $C_n(N,\beta)$ is in the exponential factor. If we multiply each term in (146) by $-\beta$ we obtain

$$-\beta u_1 > -\beta u_2 > -\beta u_3 > \cdots > -\beta u_m \tag{146'}$$

The exponential function is a monotonically increasing function of its argument. Thus

$$e^{-\beta u_1} > e^{-\beta u_2} > \cdots > e^{-\beta u_m} \tag{148}$$

Therefore the exponential factor $e^{-\beta u_1}$ dominates all others. As β grows large ($T \to 0$) the Equation (147) reduces essentially to

$$C_n(N,\beta) \simeq g_1 e^{-\beta u_1} \tag{149}$$

(149) shows that in the low temperature region the single level u_1 dictates the thermodynamic behavior. In this area the average energy $\langle u \rangle$ is

$$\langle u \rangle = -\frac{\partial}{\partial \beta}\left[-\beta u_1 + \ln g_1\right] = u_1 \tag{150}$$

From this together with Equation (105) we see that the heat capacity C_v is just the ideal gas value $nk/2$. As temperature increases the other levels begin to exert an influence which means that the value <u> will begin to increase from u_1. In the other extreme $\beta \to 0$ ($T \to \infty$) we have

$$C_n(N,\beta) = \sum_{j=1}^{N} g_j \cdot 1 \tag{151}$$

The average energy $\langle u \rangle = \frac{1}{C_n(N,\beta)} \sum_{j=1}^{N} u_j\, g_j$ and is the limit to which the energy <u> approaches as temperature goes to infinity. The behavior described here matches the results observed in the various calculations presented in the data. We can thus characterize the thermodynamic behavior by breaking consideration into three regions. The region in which (149) holds we shall call the low temperature region. The region in which (151) holds we call the high temperature or ideal gas region. The region between these two extremes we shall call the intermediate region and as is true for most intermediate situations it is the most difficult to describe. The width of the intermediate region will depend on the number of levels and the spacings. Each region is characterized by different properties. In the low temperature region the ordering of the level u_1 is imposed on the system and it is this order one sees in the correlation function. In the intermediate region the system is undergoing rapid change in the preferences for given levels. All levels now are active and contributing. In the high temperature region the system approaches asymptotically the 0 interaction gas of hard spheres. We can thus predict the behavior in both the low temperature limit and the high temperature limit.

Let us first examine the potential $V(x) = -64(\frac{2}{x})^6$ for particles of diameter 2 cells. This was examined in the treatment of the canonical ensemble. This potential has its minimum at the point of closest approach x= 2. Since V(2) is the minimum value of the potential we should expect the minimum level u_1 to be the level in which V(2) occurs most frequently. Since there are n particles the largest any value of the Profile P_j can take on is n as we have shown earlier. In order for P_2 to be equal to n every other cell must be occupied a situation which can only happen if N = 2n. For all other value of N, P_2 must be smaller or equal to n-1. There is but one array in which P_2 = n-1. That is the array in which the particles are in contact. This corresponds to the configuration

$$[1\,0\,1\,0\,1\,0\,1\,0 \cdots 1\,0\,0\,0 \cdots 0] \tag{152}$$

and all translates of it. There are N translates of this configuration, hence the multiplicity of the level is g_1 = N. The energy of this level is found from the infinite profile. The infinite profile of this configuration is given by

$$P_{2j} = n-j \quad ; \quad P_{2j+1} = 0 \tag{153}$$

Thus the energy $u_1 = \sum_{j=1}^{n-1} (n - j)[V(2j) + V(N - 2j)]$

$$\Rightarrow C_n(N,\beta) = N e^{-\beta \sum_{j=1}^{n-1} (n-j)\left[V(2j) + V(N-2j)\right]} \tag{154}$$

Let us compute the pressure from (154).

$$\beta P = \frac{\Delta C_n(ne+F,\beta)}{C_n(ne+F,\beta)} = \frac{1}{N} + \Delta e^{-\beta \sum_{j=1}^{n-1} (n-j)\left[V(2j)+V(N-2j)\right]}$$

$$= \frac{1}{N} + \left[e^{-\beta \sum_{j=1}^{n-1} (n-j)\Delta V(N-2j)} - 1\right] \tag{155}$$

From the result (155) it is clear that for large N where $\Delta V(N - 2j)$ is quite small $\beta P = 1/N$. When N is in the neighborhood 2n $\Delta V(N - 2j)$ becomes significant. From the nature of the potential the fact that it is always attractive for $x \geq 2$ indicates that $\Delta V(N - 2j) > 0$, hence for N near 2n (155) becomes

$$\beta P = \frac{1}{N} - 1 \tag{156}$$

(156) would imply that in the low temperature region, in the region in which $N = 2n$, $P = \frac{1}{N\beta} - \frac{1}{\beta}$. Refer to Figure 33. Note the behavior of P. It matches exactly the predictions of the preceeding arguments. The dotted line in that figure is a plot of $1/N\beta$. Figure 33 again

shows that for N = 2n the pressure $\simeq T = 1/\beta$ and as the volume (number of cells N) increases, the pressure approaches the asymptotic value 1/N.

The correlation function for the above system will be given by the profile which follows from (153). For our case, where n = 5 and N = 13, for example, the profile is

$$\begin{aligned} P &= (04\,0302010000) + (0\,0\,0\,0\,10203 \\ &= (04\,0312213040) \end{aligned} \tag{157}$$

Examination of the correlation function Figure 30 shows that it follows the form of (157) quite well. As the volume N changes, the profile P changes. The infinite profile does not change with N but merely adds zeros in the extra positions. The profile is the sum of the infinite profile p_j plus its mirror image so to speak p_{N-j}. Let $p_j^* = p_{N-j}$. Thus as N increases the affect of p_{N-j} on the first few components of P ceases until at large N the two are entirely separated so that the profile P is just the infinite profile up to j = N/2 and then repeats since $P_j = P_{N-j}$. This behavior can be noted in Figures 30, 31, and 32.

The plots of correlation function versus temperature suggested a relationship between the correlation function and the heat capacity. Such a relationship obviously exists since we have shown that $\text{cor}(k) = \frac{N}{n^2} \langle P_k \rangle$. The energy u of a configuration is

$$u = \sum_{j=1}^{N-1} P_j V_j \quad \text{so that} \quad \langle u \rangle = \langle \sum_{j=1}^{N-1} P_j V_j \rangle = \sum_{j=1}^{N-1} \langle P_j \rangle V_j$$

$$\langle u \rangle = \frac{n^2}{N} \sum_{j=1}^{N-1} \mathrm{cor}(j) V_j \tag{158}$$

Now there are always $\binom{n}{2} = \frac{1}{2} n(n-1)$ distinct pairs taking part in the interactions to form an energy u. Thus we have

$$\sum_{j=1}^{N-1} P_j = \frac{1}{2} n(n-1) \tag{159}$$

$$\Rightarrow \sum_{j=1}^{N-1} P_j = n(n-1) = \frac{n^2}{N} \sum_{j=1}^{N-1} \mathrm{cor}(j) \tag{160}$$

If the interparticle interaction V_j is a constant, then $u = n(n - 1)\,V$ and in fact $\langle u \rangle = n(n - 1)\,V$. The cases of interest, however, are not of the constant potential type. One can easily show that the statistics of a system are not affected by a shift in the position of the zero of the energy. Thus if we let $V_j' = V_j + V$ we have

$$\begin{aligned} C_n'(N,\beta) = \sum_{j=1}^{m} g_j e^{-\beta u_j'} &= \sum_{j=1}^{m} g_j\, e^{-\beta\{u_j + n(n-1)V\}} \\ &= e^{-\beta n(n-1)V} \sum_{j=1}^{m} g_j\, e^{-\beta u_j} \\ &= e^{-\beta n(n-1)V} C_n(N,\beta) \end{aligned} \tag{161}$$

The result in (161) shows that the change in C_n brought on by a change in the zero level is simply to multiply the partition function by a constant. This is not the case in the grand ensemble. However, one should be careful what he reads out of grand ensemble results. The energy V of course can be arbitrary. If we take V to be negative, then $e^{-\beta n(n-1)V} > 1$ and $\lim_{n\to\infty} e^{-\beta n(n-1)V} = \infty$. If we write the grand ensemble partition function $\mathcal{Q}_N(Z,\beta) = \sum_{n=0}^{N} Z^n Q_n(N,\beta)$. Suppose we now redefine the zero of the energy. Let $V_j' = V_j + V$ where $V < 0$. $\mathcal{Q}_N'(z,\beta) = \sum_{n=0}^{N} z^n Q_n'(N,\beta)$ $= \sum_{n=0}^{N} z^n e^{-n(n-1)V} Q_n(N,\beta) \geq z^N e^{-\beta N(N-1)V} Q_N(N,\beta)$. The thermodynamic limit of the grand ensemble partition function is taken as

$$\lim_{\substack{N\to\infty \\ \rho = \text{constant}}} \frac{1}{N} \ln \mathcal{Q}_N = \lim_{\substack{N\to\infty \\ \rho = \text{constant}}} \ln \mathcal{Q}_N^{1/N} \tag{162}$$

The validity of the grand ensemble is doubtful if this thermodynamic limit does not exist. We show above that

$$\mathcal{Z}_N' \geq z^N Q_N(N,\beta)\, e^{-\beta N(N-1)V} \text{ ; where } Q_N(N,\beta) = e^{-\beta N \sum_{j=1}^{N-1} V_j} \tag{163}$$

Let us take the thermodynamic limit of (163).

$$\lim_{N\to\infty} \mathcal{Z}_N'^{\frac{1}{N}} \geq \lim_{N\to\infty} z\, Q_N^{\frac{1}{N}}\, e^{-\beta(N-1)V} = \infty \tag{164}$$

Now if V is negative the limit above is infinite indicating that the whole process of redefining the zero is dangerous in the grand ensemble. It is clear that some condition must be imposed on the potential to prevent the situation shown above from occurring. It seems likely that one should require $\lim_{j\to\infty} V_j = 0$. Tross takes the potential $V(x) = -\zeta$, a constant, and shows behavior indicative of a phase transition is observed. Note, however, if we redefine the energy as $V_j' = V_j + \zeta = 0$ we are back to the Tonks gas in which no transition occurs. The considerations above therefore cast doubts on the meaning of the calculations performed. None of the interparticle forces depends on the absolute value of the energy but only on the slope. Thus the statistics cannot depend on the location of the zero energy level. We should expect to see exactly the same behavior for $V(x) = 0$ and $V(x) = -\zeta$. That the grand ensemble does not bear this out is evidence of its failure in one or the other case. We have shown that the failure occurs for $V(x) = -\zeta$ because the thermodynamic limit does not exist. Let us return to our consideration of the correlation function.

$$\langle u \rangle = \frac{n^2}{N} \sum_{j=1}^{N-1} V_j \, \mathrm{cor}(j) \qquad (158)$$

From our discussion of changing the zero level of potential we see that if we change the energy V_j by V we have

$$\langle u \rangle = \frac{n^2}{N} \sum_{j=1}^{N-1} V_j' \, \mathrm{cor}(j) - n(n-1)V \qquad (165)$$

Suppose we redefine the zero of potential so that all values V_j are negative or zero. Suppose we define it in such a way that the largest V_j is 0. With this definition we can write that

$$\langle u' \rangle = \frac{n^2}{N} \sum_{j=1}^{N-1} V_j' \, \mathrm{cor}(j) \simeq \frac{n^2}{N} (V_j')_{min} \, \mathrm{cor}(j_{min}) \qquad (166)$$

The last form shows that most of the internal energy is determined by the minimum of $V'(x)$. This shows why the internal energy $\langle u \rangle$ and the correlation functions have similar appearance. Since $V_j \leq 0$ for the potentials we use we invert the shape of correlation curve for the internal energy curve. Now the heat capacity is given by

$$C_v = \frac{nk}{2} + \frac{\partial}{\partial T}\langle u\rangle = \frac{nk}{2} + \frac{n^2}{N}\sum_{j=1}^{N-1} V_j \frac{\partial}{\partial T}\operatorname{cor}(j)$$

so that the heat capacity is largest when the correlation is changing the fastest with temperature. This is verified by the computer results.

The considerations above are quite general, applying to all types of potentials and all sized lattice systems. We have considered the potential $V(x) = 64(\frac{2}{x})^6$ and have seen that our qualitative considerations yield excellent values of the pressure and correlation functions, internal energy and heat capacity. Let us now examine the potential $V(x) = 100[(\frac{2}{x})^{12} - (\frac{2}{x})^6]$, e = 2. The repeatedly occurring nature of the value 3 or 1/3 in the results for this potential can be explained by noting that the minimum of V(x) occurs at $x = 2\sqrt[6]{2}$. As far as the lattice structure is concerned, the minimum of V(x) occurs at x = 3 since V(2) = 0. Since the strongest interaction occurs at a separation of 3 cells the lowest level u_1 will be the one in which the separation 3 occurs most often. As in the considerations for the other potentials, we note that the component P_3 of the profile is bounded by n-1 if N > 3n. For N > 3n the analysis of the previous potential carries over and we have that at N = 3n, $P = +\frac{1}{N\beta} - \frac{1}{\beta}$. This is observed in the pressure-volume curves for n = 5 at N = 15. In Figures 13 and 25 note that the minimum of the T = 1°

curve occurs at $N = 15$ and 18 respectively and is -1 approximately in both cases. For $n < 3N$ the correlation function data is irregular although peaks begin to form around $k = 3, 6$, etc. as $n \rightarrow 3N$ from below. When $N = 3n$ the peaks at 3, 6, etc. are unmistakable and indicate that the strong preference for separations of 3 cells due to the potential is strongest at $N = 3n$ as should be expected. Beyond $N = 3n$ the correlation is that of the configuration

$$[100100100\cdots1000000\cdots0] \qquad (167)$$

or its translates.

These considerations quite well explain the observed behavior and indicate the generality of the qualitative considerations. Let us now examine the results obtained from the grand ensemble. The unusual pressure-density curves can be explained simply by noting that the partition function $C_n(N,\beta)$ is not an increasing function but possesses a maximum at $n = N/3$. This is again due to the potential. For $n < N/3$ and in the low temperature region

$$C_n(N,\beta) = N e^{-\beta \sum_{j=1}^{n-1} (n-j)\left[V(3j) + V(N-3j)\right]} \qquad (168)$$

As n increases $C_n(N,\beta)$ increases until $n = N/3$. At this point the function $C_n(N,\beta)$ achieves its maximum and begins to decrease. Since $C_{N/3}(N,\beta)$ is greater than any other values around it, this one term of the grand partition function $$C_{N/3}\, e^{\beta \frac{N}{3} \sum_{j=1}^{N-1} V_j} \left[Z''^{\frac{N}{3}} + Z''^{\frac{2N}{3}} \right]$$

dominates so that $\bar{n} = N/3$ over a wide range of values of Z and then rapid change until $\bar{n} = 2N/3$ which is stable over wide range of variation of Z. Thus we expect to see a nearly vertical portion at $\rho = 1/3$ followed by a flat portion, then another vertical part at $\rho = 2/3$. That this actually occurs is shown by the results. When e = 2, $\rho \leq 1/2$ so that we observe only one vertical portion of our P-ρ curve at $\rho = 1/3$. Thus our discussion shows that the results are quite valid and in keeping with one's intuitive reasoning.

CHAPTER VI

CONCLUSION

From the theoretical work and the computer results we can conclude the following:

The scarcity of results obtained for finite systems is somewhat surprising in view of the ease of the calculations and the remarkably realistic nature of the results obtained here. The lattice system has been shown to be a useful tool in the study of the behavior of finite systems. It seems likely that a thorough understanding of such systems will aid in the study of more complex systems.

While it is true no phase transition can occur for finite systems, it is also true that the low temperature and high temperature behavior in the finite case are quite different. The computer results confirm what our theoretical arguments suggest, namely, that low temperature behavior is characterized by ordered systems and the thermodynamic behavior is characteristic of such ordered systems while at high temperature the behavior is essentially that of the Tonks gas of hard spheres of the same diameter. Our theoretical arguments show that these characteristics will obtain for any finite system. Thus it would appear that the discontinuous changes which can occur in the thermodynamic limit occur continuously over a finite temperature range in finite systems so that what one regards as a phase transition in the thermodynamic limit is spread over a finite interval in finite systems.

The treatment of small, one dimensional systems by computer gives a special insight into the behavior of such systems and suggests relationships such as the one which was found relating the energy $<u>$ to the correlation function, i.e., $<u> = \frac{n^2}{N} \sum_{j=1}^{N-1} \mathrm{cor}(j)\, V_j$. This result which we have proved for one-dimensional lattice systems is reminiscent of forms one uses to evaluate the internal energy in the continuum in three dimensional systems. The treatment of the interparticle interaction $V(x)$ as a vector quantity with the components $V_k = V(k\ell)$ has proved to be a useful concept in suggesting relations such as above. It also suggests that analogous procedures could be of value in continuum systems adding new insights into the physics of such systems.

We have indicated the dissimilarity between the results of the canonical and grand canonical ensembles, especially in the evaluation of the pressure. It is the nature of the grand ensemble that it predicts thermodynamics in agreement with the canonical ensemble results only in the thermodynamic limit. Since the grand ensemble is defined as a sum over canonical ensembles, it can have no greater validity than any of the component ensembles. Thus the predictions of the grand ensemble should not be viewed as representing with any degree of accuracy the thermodynamics of finite systems but should only be used to study the approach to the thermodynamic limit. The canonical ensemble yields answers more in keeping with ones intuitive expectations and hence should be regarded as the more fundamental. Certainly, if the canonical ensemble predicts erroneous results, the grand ensemble cannot be expected to do better.

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APPENDIX

COMPUTER PROGRAMS FOR FINITE SYSTEMS

The following two programs were used to make the computer calculations reported in this work. The important quantities were symbolized for the computer as follows:

CANONICAL ENSEMBLE STATISTICS

Variable	Name of variable in program
potential	V(I)
temperature	TEMP
number of particles	NPRT
maximum number of cells	NCLS
minimum number of free cells	MIN
particle diameter	LEX
profile	IRHO(I)
partition function	CN
pressure	PR
internal energy	EI
heat capacity	CV
correlation function	COR(I)

GRAND ENSEMBLE STATISTICS

Variable	Name of variable in program
potential	V(I)
temperature	TEMP
number of cells	NCLS

Variable	Name of variable in program
particle diameter	LEX
profile	IRHO(I)
pressure	P
density	DEN
internal energy	HN
heat capacity per cell	SPH
correlation function	COR(K)

```
C     STATISTICS OF MANY-PARTICLE SYSTEMS-CANONICAL ENSEMBLE
      DIMENSION V(50), IA(50), IRHO(50), T5(50)
      READ (1, 100) NPRT, NCLS, LEX, MT
      READ (1, 106) MIN, STEMP,FRCT
      WRITE (3, 107) NPRT
      DO 10 I=1, NCLS
      Q=2.0/I
      V(I)=100.0*(Q**12-Q**6)
   10 CONTINUE
      NEXC=NPRT*LEX
      NFC=NCLS-NEXC
      JMAX=NPRT-1
      DO 80 LTEMP=1,MT
      TEMP=STEMP+(LTEMP-1)/FRCT
      SUM=0.0
      DO 9 I=1,JMAX
    9 SUM=SUM+V(I*LEX)
      PCN=LEX*EXP(-SUM*NPRT/TEMP)
      M1=0
      DO 80 M=MIN, NFC
      LVOL=M+NEXC
      WRITE (3, 101) TEMP, LVOL, LEX
      T1=0.0
      T3=0.0
      T4=0.0
      MAX=(M+NEXC)/2
      DO 190 I=1,MAX
  190 T5(I)=0.0
      N=0
   11 N=N+1
      DO 12 J=N, JMAX
   12 IA(J)=0
   13 IS=0
      DO 14 J=1, JMAX
   14 IS=IS+IA(J)
      IA(NPRT)=M-IS
   15 J=JMAX
   16 IF(IA(J)-IA(NPRT)) 17, 17, 22
   17 J=J-1
      IF(J-1) 18, 16, 16
   18 U=0.0
      DO 185 KY=1, LVOL
  185 IRHO(KY)=0
      DO 20 JX=1, JMAX
      JN=NPRT-JX
      DO 20 KX=1,JN
      IS=0
      JK1=JX+KX-1
      DO 19 NP=JX, JK1
   19 IS=IS+IA(NP)
      IP=IS+KX*LEX
  184 IRHO(IP)=IRHO(IP)+1
      IRHO(LVOL-IP)=IRHO(LVOL-IP)+1
   20 U=U+V(IP)+V(LVOL-IP)
```

```
      Q=1.0
      DO 21 IJ=1, JMAX
   21 Q=Q+IA(IJ)/IA(NPRT)
      W=EXP(-U/TEMP)/Q
      T1=T1+W
      T3=T3+U*W
      T4=T4+U*U*W
      DO 187 KW=1, MAX
  187 T5(KW)=T5(KW)+IRHO(KW)*W
      IA(JMAX)=IA(JMAX)+1
      IA(NPRT)=IA(NPRT)-1
      GO TO 15
   22 IS=0
      JKMAX=NPRT-3
      DO 23 JK=1,JKMAX
   23 IS=IS+IA(JK)
      N=NPRT-2
   24 IA(N)=IA(N)+1
      IF(2*IA(N)+IS-M) 11,11,25
   25 N=N-1
      IF(N-1) 27, 26, 26
   26 IS=IS-IA(N)
      GO TO 24
   27 CN=(M+NEXC)*T1
      PR=TEMP*(CN-PCN)/(PCN*(M-M1))
      PCN=CN
      M1=M
      EI=T3/T1+NPRT*TEMP/2.0
      CV=NPRT/2.0+(T4-T3*T3/T1)/(T1*TEMP*TEMP)
      WRITE (3, 104) CN, PR, EI, CV
      DO 189 LK=1, MAX
      COR=T5(LK)*LVOL/(NPRT*NPRT*T1)
  189 WRITE (3, 103) COR,LK
   80 CONTINUE
      STOP
  100 FORMAT (4I6)
  101 FORMAT (' THE TEMPERATURE IS', F6.2,' THE VOLUME IS ', I4,' AND TH
     1E EXCLUSION LENGTH IS',I4)
  103 FORMAT (' CORRELATION FUNCTION = ', E16.6, 'SEPARATION = ',I4)
  104 FORMAT (' PARTITION FUNCTION = ',E16.6,' PRESSURE = ',E16.6,' INTE
     1RNAL ENERGY = ',E16.6,' SPECIFIC HEAT = ',E13.6)
  106 FORMAT(I4, 2F6.2)
  107 FORMAT (' STATISTICS OF', I4,' PARTICLE SYSTEM.')
      END
/DATA
     6    22     2    10
   1  4.00  0.25
/END
```

```
C     STATISTICS OF MANY-PARTICLE SYSTEMS-GRAND ENSEMBLE
      DIMENSION V(50), IA(50), C(50), BH1(50), BH2(50),IRHO(50),
     1PDF(50,50), T3(50), COR(50)
      READ (1, 100) NCLS, MX, LEX
      READ (1, 101) MIN, STEMP, FRCT
      DO 9 I=LEX, NCLS
      X=1.0/I
    9 V(I)=-64.0*X**6
      SUM=0.0
      LDLTA=1/LEX
      NAX=NCLS/(LEX+LDLTA)
      NM1=NCLS-LEX
      NM2=NCLS-2*LEX
      MAX=NCLS/2
      NLNS=MAX/4
      IREM=MAX-4*NLNS
      IREM1=4*NLNS+1
      DO 10 I=LEX, NM1, LEX
   10 SUM=SUM+V(I)
      DO 90 LTEMP=MIN, MX
      TEMP=STEMP+(LTEMP-1)/FRCT
      SMT=SUM*LDLTA/TEMP
      C(1)=NCLS*EXP(SMT)
      BH1(1)=.5
      BH1(NCLS)=NCLS*(SMT+.5)
      BH1(NM1)=.5*NM1+NM2*SMT
      BH2(1)=.75
      BH2(NCLS)=.25*(NCLS**2+2*NCLS)+SMT*NCLS**2+(NCLS*SMT)**2
      BH2(NM1)=.25*(NM1**2+2*NM1)+NM2*NM1*SMT+(NM2*SMT)**2
      WRITE (3,107)
      WRITE(3, 102) TEMP, NCLS, LEX
      WRITE (3,107)
      DO 80 NPRT=2, NAX
      M=NCLS-NPRT*LEX
      IF(M) 198, 198, 199
  198 T=EXP(-NPRT*SUM/TEMP)
      T1=NPRT*SUM*T
      T2=NPRT*SUM*T1
      DO 5 KW=1,MAX
    5 T3(KW)=(KW/LEX-(KW-1)/LEX)*NPRT*T
      GO TO 81
  199 T=0.0
      T1=0.0
      T2=0.0
      DO 160 KY=1, MAX
  160 T3(KY)=0.0
      NSR=NPRT+1
      IA(NSR)=M
      IA(1)=M
      N=1
   11 N=N+1
      DO 12 J=N, NPRT
   12 IA(J)=0
   13 J=NPRT
```

```
   14 IF(IA(J)-IA(NSR)) 17, 17, 22
   17 J=J-1
      IF(J-2) 18, 14, 14
   18 U=0.0
      DO 185 KY=1,NCLS
  185 IRHO(KY)=0
      DO 20 JX=2, NPRT
      JN= NSR-JX
      DO 20 KX=1, JN
      IS=0
      JK1=JX+KX-1
      DO 19 NP=JX, JK1
   19 IS=IS+IA(NP)
      IP=IS+KX*LEX
  184 IRHO(IP)=IRHO(IP)+1
      IRHO(NCLS-IP)=IRHO(NCLS-IP)+1
   20 U=U+V(IP)+V(NCLS-IP)
      Q=1.0
      DO 21 IJ=2, NPRT
   21 Q=Q+IA(IJ)/IA(NSR)
      W=EXP(-U/TEMP)/Q
      T=T+W
      T1=T1+U*W
      T2=T2+U*U*W
      DO 187 KW=1, MAX
  187 T3(KW)=T3(KW)+IRHO(KW)*W
      IA(NPRT)=IA(NPRT)+1
      IA(NSR)=IA(NSR)-1
      GO TO 13
   22 IA(NSR)=IA(NSR)+IA(NPRT)
      N=NPRT-1
   23 IA(N)=IA(N)+1
      IA(NSR)=IA(NSR)-1
      IF(IA(N)-IA(NSR)) 11, 11, 24
   24 IA(NSR)=IA(NSR)+IA(N)
      N=N-1
      IF(N-2) 81, 23, 23
   81 C(NPRT)=NCLS*T
      BUK=T1/T
      NT1=NCLS-NPRT
      NT2=NT1-NPRT
      BUNK=NT2*SUM+BUK
      BU2K=T2/T
      BU2NK=(NT2*SUM)**2+2*NT2*SUM*BUK+BU2K
      BH1(NPRT)=.5*NPRT+BUK/TEMP
      BH1(NT1)=.5*NT1+BUNK/TEMP
      BH2(NPRT)=.25*(NPRT**2+2*NPRT)+NPRT*BUK/TEMP+BU2K/TEMP**2
      BH2(NT1)=.25*(NT1**2+2*NT1)+NT1*BUNK/TEMP+BU2NK/TEMP**2
      WRITE (3, 103)  NPRT, C(NPRT)
      EXBN=EXP(NPRT*SMT)
      DO 188 KM=1,MAX
      COR(KM)=T3(KM)*NCLS/(T*NPRT*NPRT)
  188 PDF(NPRT, KM)=T3(KM)*EXBN
      DO 200 LINE=1,NLNS
      L4=4*LINE
```

```
      L3=L4-1
      L2=L4-2
      L1=L4-3
  200 WRITE (3, 105) NPRT,L1,COR(L1),L2,COR(L2),L3,COR(L3),L4,COR(L4)
      IF(IREM) 80, 80, 201
  201 DO 202 I=IREM1, MAX
  202 WRITE (3, 105) NPRT, I, COR(I)
   80 C(NPRT)=C(NPRT)*EXBN
      WRITE (3,107)
      DO 90 J=1, 30
      ZED=J/5.0
      ZEDN=ZED**NCLS*LDLTA
      ZEDN1=ZED**NM1*LDLTA
      GPF=1.0+ZEDN+C(1)*(ZED+ZEDN1)
      GPFN=NCLS*ZEDN+C(1)*(NM1*ZEDN1+ZED)
      GPFN2=NCLS*NCLS*ZEDN+C(1)*(NM1*NM1*ZEDN1+ZED)
      GPF1=ZEDN*BH1(NCLS)+C(1)*(BH1(1)*ZED+BH1(NM1)*ZEDN1)
      GPF2=ZEDN*BH2(NCLS)+C(1)*(BH2(1)*ZED+BH2(NM1)*ZEDN1)
      GPF3=ZEDN*NCLS*BH1(NCLS)+C(1)*(BH1(1)*ZED+BH1(NM1)*NM1*ZEDN1)
      DO 190 LK=1, MAX
  190 COR(LK)=ZEDN+(1.0-2.0/NCLS)*C(1)*ZEDN1
      DO 89 K=2, NAX
      ZEDK=ZED**K
      IF(NCLS*LDLTA-2*K) 82, 82, 83
   82 GPF=GPF+C(K)*ZEDK
      GPFN=GPFN+K*C(K)*ZEDK
      GPFN2=GPFN2+K*K*C(K)*ZEDK
      GPF1=GPF1+BH1(K)*C(K)*ZEDK
      GPF2= GPF2+BH2(K)*C(K)*ZEDK
      GPF3=GPF3+BH1(K)*K*C(K)*ZEDK
      DO 191 LK=1, MAX
  191 COR(LK)=COR(LK)+PDF(K,LK)*ZEDK
      GO TO 89
   83 ZEDNK=ZED**(NCLS-K)
      GPF=GPF+C(K)*(ZEDK+ZEDNK)
      GPFN=GPFN+C(K)*(K*ZEDK+(NCLS-K)*ZEDNK)
      GPFN2=GPFN2+C(K)*(K*K*ZEDK+(NCLS-K)*(NCLS-K)*ZEDNK)
      GPF1=GPF1+C(K)*(BH1(K)*ZEDK+BH1(NCLS-K)*ZEDNK)
      GPF2=GPF2+C(K)*(ZEDK*BH2(K)+ZEDNK*BH2(NCLS-K))
      GPF3=GPF3+C(K)*(BH1(K)*ZEDK*K+BH1(NCLS-K)*(NCLS-K)*ZEDNK)
      DO 192 LK=1, MAX
  192 COR(LK)=COR(LK)+PDF(K,LK)*(ZEDK+ZEDNK)+(1.0-2.0*K/NCLS)*C(K)*ZEDNK
   89 CONTINUE
      BARN=GPFN/GPF
      VARN=GPFN2/GPF-BARN**2
      P=TEMP*ALOG(GPF)/NCLS
      DEN=BARN/NCLS
      HN=GPF1/GPF
      SPH=GPF2/GPF-HN**2
      SPH=SPH-(GPF3/GPF-BARN*HN)**2/VARN
      SPH=SPH/NCLS
      HN=HN*TEMP
      DO 193 LK=1, MAX
  193 COR(LK)=COR(LK)/(GPF*DEN*DEN)
```

```
      DO 204 LINE=1, NLNS
      L4=4*LINE
      L3=L4-1
      L2=L4-2
      L1=L4-3
  204 WRITE (3, 106) L1,COR(L1),L2,COR(L2),L3,COR(L3),L4,COR(L4)
      IF(IREM) 90, 90, 205
  205 DO 206 I=IREM1, MAX
  206 WRITE (3, 106) I, COR(I)
   90 WRITE (3, 104) P, DEN, HN, SPH
  100 FORMAT (3I6)
  101 FORMAT ( I6, 2F6.2)
  102 FORMAT(' THE TEMPERATURE IS',F6.2,' THE VOLUME IS',I4,' AND THE EX
     1CLUSION LENGTH IS',I4)
  103 FORMAT (' C( ', I6, ' ) = ', E16.6)
  104 FORMAT(' PRESSURE = ', E16.6,' DENSITY = ',E16.6,' INTERNAL ENERGY
     1 = ', E16.6, ' SPECIFIC HEAT = ', E16.6)
  105 FORMAT (' NPRT = ',I3, 4(' COR(',I3,'   ) = ', E16.6))
  106 FORMAT (4(' COR(',I3,'   ) = ', E16.6))
  107 FORMAT('    ')
      STOP
      END
/DATA
    13     5     1
     1  6.00  0.50
/END
```

VITA

The author, John Roger Glaese, was born on September 6, 1942, in Jennings, Missouri. He received his primary education from the Vine Hill School in Crawford County and his secondary education from Crawford County R-II High School, Cuba, Missouri. He did his undergraduate and graduate training at the University of Missouri -- Rolla. He received a Bachelor of Science in Physics in August, 1964, and the Master of Science in Physics in May, 1966.

He has been enrolled in the Graduate School of the University of Missouri -- Rolla since September, 1964, and has held an N.S.F. Traineeship from September, 1964, to August, 1965, an N.S.F. Cooperative Fellowship from September, 1965, to August, 1966, and a N.A.S.A. Traineeship from June, 1966, to September, 1967.

He was married in January, 1967, to the former Miss Carolyn Allemann of New Florence, Missouri.