1957

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Recommended Citation

Mukerjee, Hari Gopal, "Some thermodynamic and structural properties of a linear chain of atoms, and extension of the model to two- and three-dimensional cases" (1957). *Masters Theses*. 2558.
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SOME THERMODYNAMIC AND STRUCTURAL PROPERTIES OF A LINEAR CHAIN OF ATOMS, AND EXTENSION OF THE MODEL TO TWO- AND THREE-DIMENSIONAL CASES

BY

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A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE, PHYSICS MAJOR

Rolla, Missouri

1957

Approved by -
Professor of Physics

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LIST OF ILLUSTRATIONS

ACKNOWLEDGEMENT

The author takes pleasure in acknowledging his indebtedness to Mr. L. H. Lund of the department of Physics, MO School of Mines and Metallurgy, without whose invaluable help ans assistance the work would not have been realized.

INTRODUCTION

The explanation of thermodynamic and other properties of matter, solids, liquids, and gases, from the atomistic point of view, has been one of the most extensively investigated fields of Physics and Chemistry during the modern history of science. Gases and solids were always given more importance because their properties are amenable to explanations, at least crudely, based on some simple idealized assumptions. Not until in comparatively recent times have liquids been able to attract much attention from scientists. In this background, naturally, attempts at correlation of the properties, especially structural, of the three states of matter have not been ample. With the advent of x-ray analysis the question as to the existence of any correlation at all has been answered conclusively in the affirmative. But the exact quantitative relationships have not been found in any general case. The task is not an easy one. We have three distinct thermodynamically stable phases with properties almost uniformly varying with temperature, separated by two discontinuities corresponding to the melting and boiling points. Additional comlications are encountered when we consider some properties that undergo practically no change on phase transformation.

According to the classical view the solid was considered to be an array of atoms rigidly held to fixed relative positions in space, and the liquid was considered to be a reapproximated gaseous state. The modern conception of the liquid state — at temperatures lying near the crystallization point — is very similar to that of the solid state. The apparent opposition between these two phases have been removed by the discovery of elements of rigidity and order in the liquid state on the one hand, and fluidity and disorder in the solid state on the other. The structures of the liquid and the solid states thus must not be essentially different, and the theory of the liquid state must be developed in the same line as that of the solid state.

Joffe(1) was the first one to introduce the conception of a partial dissociation of the lattice and the notion of heat motion as an alternative to small vibrations of atoms about fixed equilibrium positions in space into the kinetic theory of crystals. This has led to the correct understanding of molecular-kinetic motions of molecules in both the solid and the liquid states as a motion of vibration-diffusion type, the diffusion being more pronounced in the liquid state in as much as the equilibrium positions of the atoms are more randomly distributed.

It was believed, however, until the time of the pio-

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(1) Joffe, A., Ann. d. Phys., 72 (1923) 461.

neering experiments of Stewart(2) with the x-ray scattering of liquids that there is a total absence of arrangement and order of atoms in the liquid state. Stewart's experiments have shown that liquids near the crystallization temperature exhibit a large amount of local order, and the structural difference between the solid and the liquid states is more of a quantitative than qualitative nature.

According to the modern conception, atoms in a crystalline solid are arranged in a self-consistent field of potential energy set up by the atoms themselves, and executing small thermal vibrations about their equilibrium positions determined by the fields of their neighbours, thus displaying a long range or distant order. The range of the vibrations of the atoms (root-mean-square value) increases monotonously with temperature. Thus the probability of finding an atom outside its equilibrium position becomes higher, causing more and more vibration-diffusion with loss of order in the substance. Near the melting point the change is greatly accelerated, acquiring a more pronounced "co-operative" character in the sense that it requires less and less energy for further decrease of order. The thermal expansion (at constant pressure) and the accompanying increment in the value of the interatomic distances is a further cause enhan-

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(2) Stewart, G. W., Phys. Rev., 30 (1927) 232; 31 (1928) 174; 35 (1930) 726; 37 (1931) 9.

cing loss of order. The increase of volume on fusion is simultaneously the direct cause and effect of this loss. The long range order breaks down on melting and the liquid shows a short range or local order near the melting point, thus exhibiting a quasi-crystalline structure. With still further increase of temperature the liquid assumes a more and more gas-like state until the boiling point is reached. Osida(3) and others have tried to consider a solid as an arrangement of atoms with fixed equilibrium positions while a liquid, near the crystallization point, is an array of atoms whose equilibrium positions are determined by the positions of their neighbours. This is clearly fallacious since the positions of the atoms cannot be independent of the others.

Even with all the advancement and the voluminous amount of work put out in recent times, the theory of the liquid state and its relation with the solid state is still in a very elementary form. A successful model has not been found even for the simplest types of liquids like fused metals. The various special types of molecular structures and molecular forces are added complications to the yet unsolved problem. All attempts are based on the method of the partition sum which, in itself, is not objectionable. However, the efforts of Mayer, Ackermann, Born, and Fuchs in

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(3) Osida, I., Prc. Phys.-Math. Soc., Japan, 25 (1943) 582.

the late thirties and early forties(4) to evaluate the partition sum in a rigorous way leads to extremely complicated mathematics. On the other hand, the so-called cell method of Lennard-Jones and Devonshire, Eyring and others,(5) which leads to numerically satisfactory results, are subject to serious objections.

An attempt has been made in the present work to derive some thermodynamic and structural properties of a linear chain of atoms (under somewhat idealized conditions) moving in the fields of nearest neighbours and assuming a parabolic well in the interaction of pairs within the range of relative movements. The equation of state and other formulas derived are applicable only to the linear model which could be considered as a simplified form of one-dimensional crystals in the form of chain-like molecules of rubber-like substances. An attempt has also been made to extend the model to two- and three-dimensional cases.

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(4) Mayer, J. E., J. Chem. Phys., 5 (1937) 68; Mayer, J. E., and Ackermann, P. G., Ibid, 5 (1937) 74; Born, M., and Fuchs, K., Proc. Roy. Soc., A166 (1938) 391.

(5) Eyring, H., J. Chem. Phys., 4 (1936) 283; Newton, R., and Eyring, H., Trans. Faraday Soc., 33 (1936) 73; Eyring, H., and Hirshfelder, J., J. Phys., 41 (1937) 249; Lennard-Jones, J. E., and Devonshire, A. F., Proc. Roy. Soc., A163 (1937) 53; A 165 (1938) 1.

REVIEW OF LITERATURE

In calculating the partition function, distribution function and other thermodynamic and structural properties of solids and liquids, various uncertain factors, such as the type of model used, the nature of interaction among the molecules, etc., creep in, thus necessiating the results to be expressed in terms of parameters that often lose their physical meaning. It is customary to consider solid atoms being permanently distinguishable in as much as they are attached to fixed equilibrium positions in the lattice. This enables Boltzmann statistics to be employed in evaluation of the partition function.

From the classical partition function of the solid the specific heat at constant volume comes out to be 3R per mole at all temperatures and for all solids, R standing for the gas constant.

Einstein(6) considered the solid to be an array of atoms executing independent simple harmonic motions about their fixed equilibrium points in the lattice (the "lattice gas model"), to which he applied Boltzmann statistics after quantizing the energy levels of the harmonic oscillators. The resultant specific heat expression reduced to the classical value at high temperatures and to zero at absolute zero in agreement with the third law of thermodynamics. Although

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(6) Einstein, A., Ann. d. Phys., 22 (1907) 180.

this was a great improvement over the classical theory, quantitatively it is not possible to find a single value of the frequency of the oscillator to give an accurate agreement with the obsereved heat capacity over the whole temperature range. Moreover, the model itself is extremely crude and inconsistent with the modern conception.

Debye has considered a solid as an elastic continuum, imitating the actual crystal in elastic properties, and set up the partition function from the sum of the eigenvalues of the normal modes of the coninuum model with an arbitrary cut-off frequency(7). The heat capacity is expressed in terms of a single parameter, the Debye temperature, which is characteristic of the nature of the substance. At temperatures much higher than this temperature the specific heat reduces to the classical value, while at low temperatures it shows a T^3-dependence, where T is the absolute temperature. The low temperature heat capacity is very well borne out by experiment, and is one of the major successes of the Debye theory. The Debye model, however, is powerless in predicting the equation of state — pressure, volume, temperature relation. There are also many minor and major exceptions that can be understood in terms of deviations of the normal mode spectrum from that of the Debye continuum model. As has been

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(7) Debye, P. P., Ann. d. Phys., 39 (1912) 789.

shown by Blackmann,(8) the spectral density in actual crystals is at large variance with the frequency-square dependence derived by Debye. Moreover, the individual atoms lose their identities in this model, and the whole idea of substitution of an elastic continuum for for a set of discrete particles is decidedly idealistic.

Born and von Karman(9) obtained, taking into consideration the interaction of atoms with nearest and next nearest neighbours, superficially the same results as Debye, but with much more laborious computation. Although this theory is much more exact and realistic, there are too many as yet unknown effects to be taken into consideration before we can expect it to give exact predictions.

The computation of the partition function of the liquid is beset with more complexities because of the lack of a proper model. As has been stated before, the attempts at an exact evaluation of the partition function of the liquid lead to complicated mathematical entanglements. In the so-called cage model, the liquid is pictured as differing from the solid only in the circumstance that its atoms are not permanently attached to the equilibrium lattice sites, but are confined to small regions or cages by their neighbours from which they frequently leak out. The partition function

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(8) Blackmann, M., Proc. Roy. Soc., A159 (1937) 416.

(9) Born, M., and von Karman, Th., Phys. Z., 13 (1912) 297.

is set up as in the solid model of Einstein and is multiplied by an arbitrary factor to take into account the leakage mobility of the atoms from cage to cage. Kirkwood(10) has shown how this extra factor arise theoretically in the partition function of the liquid, although most investigators add the communal entropy term empirically to give the correct results. It can be shown(11) that the partition function of the liquid takes the form:

$Q_L = (1/N!)N^N Q_C \approx e^N Q_C$, using Sterling's approximation, where N is the total number of atoms in the assembly, and Q_c is the configurational integral expressing the partition function of an Einstein's solid with N atoms.

Several models closely related with the above formalismhave been proposed. Numerically, all of them give satisfactory results, but only partially so. It is interesting to review the expressions for change in entropy on fusion obtained on the basis of some common models.

We can expect an increment in entropy on melting even if the structure of the solid remains unchanged because of the volume dilation associated with fusion. But this does not amount to more than only about one-third of the total

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(10) Kirkwood, J. G., J. Chem. Phys., 19 (1951) 658.

(11) Band, W., "Quantum Statistics", D. Van Nostrand Co. Inc., N. J., 1955, pp. 131 – 134.

change in entropy as shown by Slater,(12) and in a more rigorous manner by Gruneisen.(13)

Mott(14) has attributed the large change in entropy to the change in the frequency of vibration of the atoms. But this cannot account for all of it unless there is some essential change in structure, as pointed out by Toda.(15)

Lennard-Jones and Devonshire(16) have imagined the crystal lattice as consisting of an alloy of the atoms and the inter-lattice vacant sites or holes. The phenomenon of melting has then been treated as a sort of order-disorder transition in solid binary alloys. The change in entropy on breakdown of order, which they have imagined to occur at the melting point, comes out to be R(3/2)ln 2 per mole. This explanation, however, seems to be considerably artificial, apart from the fact that the large number of holes

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(12) Slater, J. C., "Introduction to Chemical Physics", McGraw-Hill Book Company Inc., N. Y., 1939, 261.

(13) Gruneisen, G., Ann. d. Phys., 39 (1912) 302.

(14) Mott, N. F., Proc. Roy. Soc., A146 (1934) 465.

(15) Toda, M., Proc. Phys.-Math. Soc., Japan, 23 (1941) 252

(16) Lennard-Jones, J. E., and Devonshire, A. F., Proc. Roy. Soc., A169 (1939) 317; A170 (1939) 464.

necessary in the solid state to fit this scheme will make the density considerably lower. Peek and Hill(17) have tried to modify this model necessiating fewer holes.

According to the cage model of Eyring and others, the increment in entropy on breakdown of distant order is R, instead of 1.04 R as calculated by Lennard-Jones and Devonshire. The arbitrariness in the original theory of Eyring has been removed to a large extent by Gurney and Mott(18) and other investigators who put the conception of communal entropy on a firmer basis.

Osida(19) has imagined the solid as an array of atoms performing small vibrations about their equilibrium positions, and independent of the other atoms, while in the liquids the atoms have been supposed to occupy similar lattice sites, but this time moving in the fields of their immediate neighbours. Using a Gaussian distribution function to such assemblies he set up the partition function of the solid and the liquid. The resulting change in entropy is found to consist of three parts: due to the change in the static potential accompanied by the voluminal expansion; the decrement

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(17) Peek, H. M., and Hill, T. L., J. Chem. Phys., 18 (1950) 1252.

(18) Gurney, R. W., and Mott, N.F., Ibid, 6 (1938) 222.

(19) Osida, I., op. cit.

of the interatomic frequency; and due to the disappearance of the long range order in the liquid phase, the last component being the same as derived by Lennard-Jones and Devonshire. However, Osida's model of the solid suffers from the same objections as Einstein's lattice gas model.

Proper models of the solid and the liquid states must take into account the different degrees of order in the two phases. The relative distribution function, which is defined as the average number of atoms per unit volume at a distance r from an arbitrary central atom, shows very strong maxima for solids near the central atom, causing corresponding strong diffraction maxima in x-ray scattering. This is attributed to the long range order in solids. X-ray diagrams of liquids show an absence of rays scattered at small angles (as in the case of gases), but are characterized by the presence of one or more intensity maxima in the form of diffuse diffraction rings (Fig. 1). This is attributed to the pre-

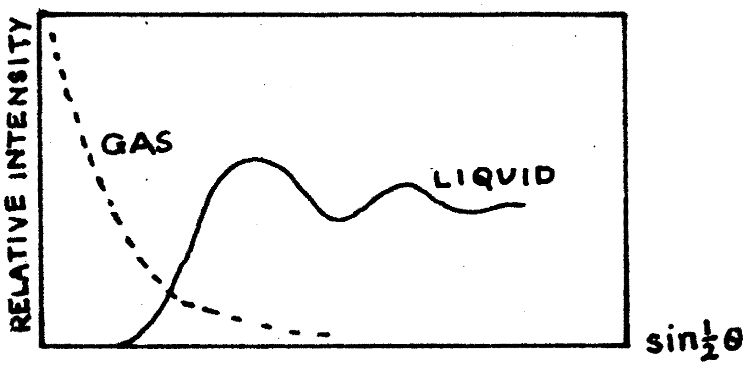

Fig. 1.

sence of short range order in liquids. The corresponding distribution function should also show broad maxima near the central atom before they attenuate to the constant value of the atomic density of the substance.

The relative distribution function $\rho(r)$ for Einstein's model of the solid is given by:

$$\rho(r) = \frac{1}{4\pi r^2} \sum_s \frac{n_s}{\sqrt{(2\pi \overline{\xi_s^2})}} e^{-(r-r_s)^2/2\overline{\xi_s^2}}$$

where n_s is the mean number of atoms at a distance of r_s from the central atom, and ξ_s is the displacement of an atom from its mean position in space. Provided the liquid is a simple (monatomic) one with a quasi-crystalline structure, the relative distribution function can be found in a similar way, as pointed out by Prins,(20) if the width of the successive Gaussian curves is increased as the square-root of the distance r_s. Basing his arguments on the free volume of a substance Kirkwood(21) has been able to derive an expression for the relative distribution function. In the case of liquids it shows an exponential damping of the density oscillations. Numerically the results are quite satisfactory for some simple liquids, but Kirkwood's arguments imply a number

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(20) Prins, J. A., Naturwissenschaften, 19 (1931) 435.

(21) Kirkwood, J. G., J. Chem. Phys., 7 (1939) 919.

of assumptions and simplifications which render questionable the physical meaning of the results obtained.

The structure diffusion constant, specifying the amount of disorder in a substance, has been computed by Prins(22) for a linear chain of atoms using a Gaussian distribution function. It is given by the expression:

$$D = \frac{\overline{\xi_s^2}}{2r_s} = \frac{kT}{2df}$$

where d is the mean interatomic distance and f is the co-efficient of the quasi-elastic force between two neighbouring atoms. Prins tried to identify the linear crystal with the three-dimensional liquid which is wholly fallacious from the structural point of view.

Following the method of Debye in the theory of specific heat of the solid, Peierls(23) has computed the mean quadratic fluctuation of the atoms due to heat motion in one-, two- and three-dimensional solids. At large distances this came out to be:

$\overline{\xi_s^2}$ = (constant)r in one-dimensional case,

= const. + (const.)ln r in two-dimensional case,

= constant in three dimensional case.

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(22) Prins and Petersen, Physica, 3 (1936) 147.

(23) Peierls, R., Helv. Phys. Acta, Suppl., ii, 81 (1936).

From this Frenkel(24) argues that the cause of the structure diffusion of liquids must not be directly connected with the heat motion, and must be an explicit function of the volume only. Peierls's findings are, however, are subject to the same objections as Debye's model of the solid.

It may be mentioned here that even with considerable quantitative agreement between theoretical and observed values many theories cannot be considered as conclusive, such numerical agreements being easily obtained by a proper choice of the parameters involved.

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(24) Frenkel, J., "Kinetic Theory of Liquids", Dover Publications, Inc., N. Y., (1946) 120.

THE SOLID AND LIQUID MODELS

In view of what has been discussed already it is quite apparent that the structures of a substance in the solid and the liquid states near the melting point are very similar. So it is but natural that for discussion of properties near the melting point the models should be essentially the same, but with different structural constants. For simplification we will further assume the interaction of atoms with those lying beyond the nearest neighbours is negligible, and the range of heat motion of an atom relative to its nearest neighbours is small so that Hooke's law is applicable. This of course does not take into consideration the anharmonic terms that come into play at high temperatures. Boltzmann statistics is employed in both the cases assuming distinguishability of the atoms. This is a fairly correct approximation for liquids lying very near the crystallization point since the rate of vibration of the atoms is much larger than the rate of migration. The degree of order in the two different states is thus attributed only to the frequency of vibration of the atoms due to heat motion.

THE ONE-DIMENSIONAL MODEL

THE PARTITION FUNCTION

First we start with a one-dimensional model in which N atoms or molecules are joined together in one line and are constrained to move in that line. Let the mean interatomic distance be d, the atomic diameter σ, and the mean clearence between two neighbouring atoms be l_0, so that

$$d = l_0 + \sigma$$

If we consider the atoms as hard spheres and if the interchange of positions of any two atoms in the assembly does not have any macroscopic effect, then the partition function of the assembly will be given by, according to Boltzmann statistics,

$$z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}} \underbrace{\int\int\cdots\int}_{N} e^{-\frac{W(x_1, x_2 \ldots x_N)}{kT}} dx_1 dx_2 \cdots dx_N \int dy$$

subject to $y = Nd + \sum_{i=1}^{N} x_i$, where x_i denotes the displacement of the ith atom from its mean position with respect to (i-1)th atom, W is the potential energy of the system expressed as a function of the co-ordinates x_i's, the kinetic part being given by

$$\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}},$$

and y is the distance of the Nth atom from the zeroeth or t the reference atom (Fig. 2), the integrations being taken

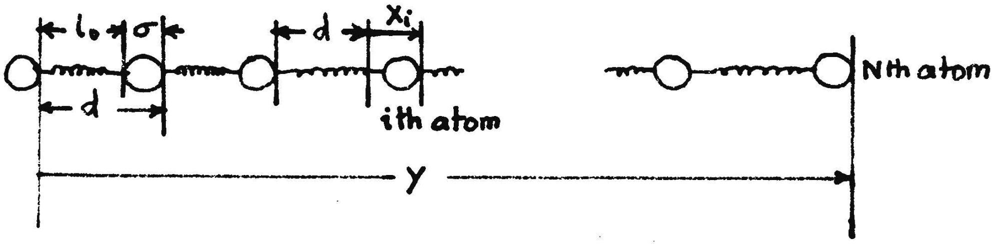

Fig. 2.

over all configuration space.

We can use the last condition as follows:

Construct $\lambda = \frac{dy}{2\pi}\int_{-\infty}^{\infty} e^{j[y-Nd-\sum_i x_i]u}\,du$, $j = \sqrt{(-1)}$

which is the Dirac delta-function, $\delta[y-Nd-\sum_i x_i]$, multiplied by dy that gives

$$\lambda = 1, \text{ when } \quad y-\frac{dy}{2} < Nd+\sum_i x_i < y+\frac{dy}{2}$$

$$= 0, \text{ when } \quad |y-Nd-\sum_i x_i| > \frac{dy}{2}$$

If the dependence of the potential energy on all the coordinates is the same and the limits of integrations are the same, then on multiplication by δ, the partition function takes the form:

$$z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}}\frac{1}{2\pi}\iint\cdots\int e^{-\frac{W}{kT}+j(y-Nd-\sum_i x_i)u}\,dx_1 dx_2\cdots dx_N\,du\,dy$$

$$= \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}}\frac{1}{2\pi}\iint\cdots\int e^{-\frac{W}{kT}+ju\sum_i x_i}\,dx_1 dx_2\cdots dx_N\, e^{j(y-Nd)u}\,du\,dy$$

$$= \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}}\frac{1}{2\pi}\int_{N\sigma}^{L} F(y)\,dy$$

where L is the length of the chain and F(y) is given by,

$$F(y) = \int_{-\infty}^{\infty} e^{j(y-Nd)u} \left[\gamma(u)\right]^{N} du$$

$$\gamma(u) = \int e^{-\frac{W}{kT} + jux_i} dx_i$$

This is the general formulation of the problem, the exact form of the partition function being dependent on the function $W(x_i)$.

The general nature of interaction between a pair of atoms is shown in the following $W(x)$ diagram, where x is the

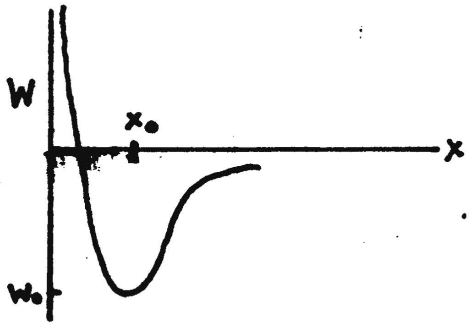

Fig. 3.

distance between the atoms. It can be seen that the mean interatomic distance at any particular temperature will be a constant (x_0), which is d in our case. Near the bottom of the well, i. e., when the thermal vibrations of the atoms are small, the curve is parabolic. The atoms will thus execute simple harmonic motions about x_0, the potential being

$$W = w_0 + (1/2)K(x-x_0)^2$$

where K is the co-efficient of the quasi-elastic force. Thus the chain of atoms can be replaced in our model by a chain of hard spheres joined together by springs of stiffness constant K (see Fig. 2), if the interaction among atoms is assumed to be confined to immediate neighbours, and the magnitude of vibration is small.

The transform $\mathcal{T}(u)$ will now be given by,

$$\mathcal{T}(u) = e^{-\frac{W_0}{kT}} \int e^{-\frac{K}{2kT}x_i^2} e^{jux_i}\, dx_i$$

If K is large, which is the case with both solids and liquids, the exponential under the integral sign will approach zero very rapidly, and the limits of integration can be taken to be from $-\infty$ to $+\infty$, so that $\mathcal{T}(u)$ will become:

$$\mathcal{T}(u) = e^{-\frac{W_0}{kT}} \int_{-\infty}^{\infty} e^{-\beta x_i^2} e^{jux_i}\, dx_i \text{ , where } \beta = \frac{K}{2kT}$$

$$= e^{-W_0/kT} \int_{-\infty}^{\infty} e^{-\beta x_i^2} \cos(ux_i)\, dx_i$$

$$= e^{-W_0/kT} \sqrt{\frac{\pi}{\beta}}\, e^{-u^2/4\beta}$$

Then,

$$F(y) = e^{-\frac{W_0}{kT}} \left(\frac{\pi}{\beta}\right)^{\frac{N}{2}} \int_{-\infty}^{\infty} e^{-\frac{Nu^2}{4\beta}} e^{j(y-Nd)u}\, du, \quad W_0 = Nw_0$$

$$= e^{-\frac{W_0}{kT}} \left(\frac{\pi}{\beta}\right)^{\frac{N}{2}} 2\sqrt{\frac{\pi\beta}{N}}\, e^{-\frac{\beta}{N}(y-Nd)^2}$$

The partition function will then take the form:

$$z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}}\left(\frac{\pi}{\beta}\right)^{\frac{N-1}{2}}\frac{1}{\sqrt{N}}\,e^{-\frac{W_0}{kT}}\int_{N\sigma}^{L} e^{-\frac{\beta}{N}(y-Nd)^2}dy$$

$$= e^{-\frac{W_0}{kT}}\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}}\left(\frac{\pi}{\beta}\right)^{\frac{N-1}{2}}\frac{1}{\sqrt{N}}\sqrt{\frac{N}{\beta}}\int_{-\sqrt{\frac{\beta}{N}}Nl_0}^{\sqrt{\frac{\beta}{N}}(L-Nd)} e^{-x^2}dx$$

$$= e^{-\frac{W_0}{kT}}\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{N}{2}}\left(\frac{\pi}{\beta}\right)^{\frac{N}{2}}\frac{1}{2}\left[\mathrm{erf}\sqrt{\frac{\beta}{N}}(L-Nd)+\mathrm{erf}\sqrt{\frac{\beta}{N}}Nl_0\right]$$

where $\mathrm{erf}(a) = \frac{2}{\sqrt{\pi}}\int_0^a e^{-x^2}dx$

FREE ENERGY AND EQUATION OF STATE

The Gibbs Free Energy, when the partition function is derived from Boltzmann statistics, is given by,

$$A = -kT \ln z$$

$$= -kT\left[\frac{N}{2}\ln\frac{2\pi mkT}{h^2}+\frac{N}{2}\ln\frac{\pi}{\beta}-\ln 2-\ln N!-\frac{W_0}{kT}+\ln\left\{\mathrm{erf}\sqrt{\frac{\beta}{N}}(L-Nd)+\mathrm{erf}\sqrt{\frac{\beta}{N}}Nl_0\right\}\right]$$

The equation of state is given by,

$$P = -\left(\frac{\partial A}{\partial L}\right)_T$$

$$= kT\;\frac{\frac{\partial}{\partial L}\left[\mathrm{erf}\sqrt{\frac{\beta}{N}}(L-Nd)+\mathrm{erf}\sqrt{\frac{\beta}{N}}Nl_0\right]}{\left[\mathrm{erf}\sqrt{\frac{\beta}{N}}(L-Nd)+\mathrm{erf}\sqrt{\frac{\beta}{N}}Nl_0\right]}$$

$$= kT\sqrt{\frac{\beta}{N}}\;\frac{\mathrm{erf}'\sqrt{\frac{\beta}{N}}(L-Nd)}{\left[\mathrm{erf}\sqrt{\frac{\beta}{N}}(L-Nd)+\mathrm{erf}\sqrt{\frac{\beta}{N}}Nl_0\right]}$$

where P is the thermal pressure exerted by the end molecule in the chain. The asymptotic expansion of erf(x) near x = 0 is given by,

$$\mathrm{erf}(x) = (2/\sqrt{\pi})(x - x^2/2 + x^3/3 - + \cdots)$$

In the limiting case when beta approaches zero, we can take only the first term of the expansion, and the equation of state is reduced to

$$P = kT\sqrt{\frac{\beta}{N}}\,\frac{2/\sqrt{\pi}}{\frac{2}{\sqrt{\pi}}\sqrt{\frac{\beta}{N}}\,(L - Nd + Nl_0)}$$

$$= kT/(L - N\sigma)$$

which is the familiar gas law, $L - N\sigma$ standing for the free volume of the substance.

SPECIFIC HEAT

The total internal energy of the system is given by,

$$E = kT^2\left(\frac{\partial \ln z}{\partial T}\right)_V$$

$$= NkT + W_0,$$

if we neglect the factor $(\sqrt{\pi}/2)(\mathrm{erf}\sqrt{\frac{\beta}{N}}(L-Nd) + \mathrm{erf}\sqrt{\frac{\beta}{N}}Nl_0)$ as being very nearly equal to one.

The specific heat at constant volume will then be give by,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = Nk$$

which is the classical expression for specific heat on the basis of equipartition of energy and not considering the quantum effects.

CHANGE IN ENTROPY ON FUSION

The entropy of a substance is given by,

$$S = k \ln z.$$

The change in entropy on fusion will then be given by,

$$\Delta S = k(\ln z_l - \ln z_s)$$

where z_l and z_s are partition functions for the liquid and the solid phases respectively.

$$\therefore \Delta S = k \ln \left[e^{(W_{0s} - W_{0l})/kT} \left(\frac{\beta_s}{\beta_L}\right)^{\frac{N}{2}} \frac{\left\{\operatorname{erf}\sqrt{\frac{\beta}{N}}(L-Nd) + \operatorname{erf}\sqrt{\frac{\beta}{N}}\,Nl_0\right\}_L}{\left\{\operatorname{erf}\sqrt{\frac{\beta}{N}}(L-Nd) + \operatorname{erf}\sqrt{\frac{\beta}{N}}\,Nl_0\right\}_s} \right]$$

$$= \frac{W_{0s} - W_{0L}}{T} + \frac{1}{2} Nk \ln \frac{\beta_s}{\beta_L} + k \ln \frac{\left\{\operatorname{erf}\sqrt{\frac{\beta}{N}}(L-Nd) + \operatorname{erf}\sqrt{\frac{\beta}{N}}\,Nl_0\right\}_L}{\left\{\operatorname{erf}\sqrt{\frac{\beta}{N}}(L-Nd) + \operatorname{erf}\sqrt{\frac{\beta}{N}}\,Nl_0\right\}_s}$$

if we neglect 1 when $N \gg 1$. Since the last term is negligible compared to the rest,

$$\Delta S = (W_{0s} - W_{0l})/T + (1/2)Nk \ln (\beta_s/\beta_l)$$

It may be noted that there is no component to the change in entropy due to loss of distant order in an explicit form because our contention is that order, in both the solid and the liquid states, is a direct function of the frequency of heat motion of the atoms, and as such the change in entropy associated with breakdown of distant order is taken care of by the frequency term in the expression.

Objection may be raised as to the validity of the liquid model on the ground that liquid atoms are capable of migrating, and hence do not have any fixed lattice sites permanently. But the same is true for solids also, especially near the melting point. Since there is no known way of computing the entropy due to migration of atoms in the solid state, and since this component of entropy is small, both in solids and liquids, it seems that the derived expression for ΔS is nearly correct, although the individual entropies, S_s and S_l, should be slighlty higher. Moreover, according to the author, the loss of distant order on fusion due to the mobility of the atoms seems to have been overemphasized, especially in temperature ranges near the crystallization point. According to the cage model or the hole theory of the liquid atoms have been pictured as too mobile. If we consider the resulting entropy due to this mobility, the ratio β_s/β_l becomes nearly one, whereas the compessibility data show that it should be nearer 2 or 3, which, incidentally, will account for the change in entropy usually attributed to the extra mobility of the atoms in th the liquid state.(25) Our theory may make the liquid seem too rigid. But there are elements of rigidity in liquids, masked by their fluidity. This is especially obvious in the case of such substances as under the influence of cooling pass from the liquid state to the solid amorphous state without crystallization, and in a continuous manner.

RELATIVE DISTRIBUTION FUNCTION

The relative distribution function, as has been defined before, expresses the average number of atoms in a

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(25) Frenkel, J., op. cit., p. 100; p. 138.

substance as a function of the distance from the reference atom. Naturally, this can be written as a sum of the probability distribution functions for all the atoms in the assembly relative to the reference atom. These individual distribution functions will now be obtained in a similar way the partition function was derived.

Referring back to Fig. 2 (page 18), the probability that the jth atom (j = 1,2,3,...N) will be found at a distance y from the reference atom is given by, according to Boltzmann distribution law,

$$P_j(y) = \left(\frac{\beta}{\pi}\right)^{\frac{j}{2}} \int\int\cdots\int e^{-\beta\sum_{i=1}^{j} x_i^2}\, dx_1\, dx_2 \cdots dx_j$$

subject to $y = jd + \sum_{i=1}^{j} x_i$, where the distribution functions are the normalized potential energy functions used in the partition function.

Using the same sort of artifice as in the derivation of the partition function and using the same sort of logic, we get, on multiplication by the Dirac delta-function,

$$P_j(y) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\sqrt{\frac{\beta}{\pi}}\int_{-\infty}^{\infty} e^{-\beta x_i^2} e^{i u x_i}\, dx_i\right]^j e^{i(y-jd)u}\, du, \quad i = \sqrt{-1}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ju^2/4\beta}\, e^{i(y-jd)u}\, du$$

$$= \sqrt{\frac{\beta}{\pi}}\,\frac{1}{\sqrt{j}}\, e^{-\frac{\beta}{j}(y-jd)^2}.$$

Thus the probability distribution curve for each atom is a

Gaussian function about its mean position with respect to the reference atom (Fig. 4), the width of the spread increasing as the square-root of the distance from the reference atom of its mean position. The integration of $P_j(y)$ from $-\infty$ to $+\infty$ yields 1 in accordance with the physical meaning of probability.

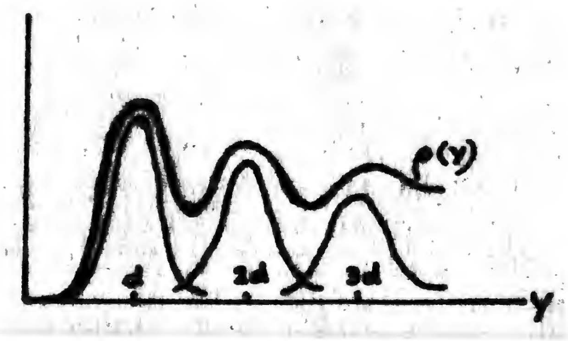

Fig. 4.

The relative distribution function will be the sum of the individual distribution functions $P_j(y)$'s (the heavy line in Fig. 4):

$$\rho(y) = \sqrt{\frac{\beta}{\pi}} \sum_{j=1}^{y/\sigma} \frac{1}{\sqrt{j}} e^{-\frac{\beta}{j}(y-jd)^2}$$

The upper limit of the sum is y/σ, because only that many atoms can be squeezed into the section y. $\rho(y)$ shows maxima near d, 2d, etc., instead of σ, 2σ, etc., as found by Kirkwood using Clausius-type distribution.

The summation of the individual distribution functions must be done numerically for small values of y. For large values of y, $\rho(y)$ tends to ρ_0, a constant equal to the mean atomic density of the substance, which in our case is 1/d. This can be shown as follows:

For large values of y/σ the summation can be replaced by an integration,

$$\rho(y) \doteq \int_1^{y/\sigma} \sqrt{\frac{\beta}{\pi}} \frac{1}{\sqrt{j}} e^{-\frac{\beta}{j}(y-jd)^2} dj$$

On substitution x = y − jd, the expression becomes,

$$\rho(y) \doteq -\sqrt{\frac{\beta}{\pi d}} \int_{y-d}^{y(1-d/\sigma)} \frac{1}{\sqrt{y-x}} e^{-\frac{\beta d}{y-x}x^2} dx$$

$$\doteq -\sqrt{\frac{\beta}{\pi d}} \int_{-\infty}^{\infty} \frac{1}{\sqrt{y}} e^{-\frac{\beta d}{y}x^2} dx \qquad = 1/d,$$

since for large values of y there is practically no contribution to the integrand from large values of the variable.

It can be seen that the number of well- distinguished maxima depends on β or the stiffness constant of the spring. Solids, having large values of β, will show a large number of sharp maxima, displaying a distant order. In liquids, with much smaller values of β, there will be only a few diffuse maxima, and will thus show only a local order. The different degrees of order in the solid and the liquid phases can thus be attributed to the difference in frequency of heat motion of the atoms, at least near the melting point. The migration of atoms in the lattice will of course make the maxima a little more diffuse than the maxima pictured here.

STRUCTURE DIFFUSION CONSTANT

The structure diffusion constant, specifying the degree of disorder in a substance, can be defined in our case as

$$D = \frac{\overline{x_j^2}}{2y_j} \text{, where } \overline{x_j^2} = \frac{1}{2\pi}\left[\int_{-\infty}^{\infty} e^{-\frac{\beta}{j}(y-jd)^2}\,dy\right]^2 \quad \text{and } y_j = jd$$

$$\therefore D = \frac{1}{2\pi}\,\frac{j\pi}{\beta}\,\frac{1}{2jd} = \frac{1}{4d\beta}$$

which is the same expression as derived by Prins.

This constant D is applicable only to the one-dimensional case, and the attempt by Prins to identify it with the structure diffusion constant of a three-dimensional liquid is clearly fallacious from the structural point of view.

TWO-DIMENSIONAL MODEL

The partition function for a simplified two-dimensional model can be set up in the following manner. Let the lattice be a square one (Fig. 5), and let the potential

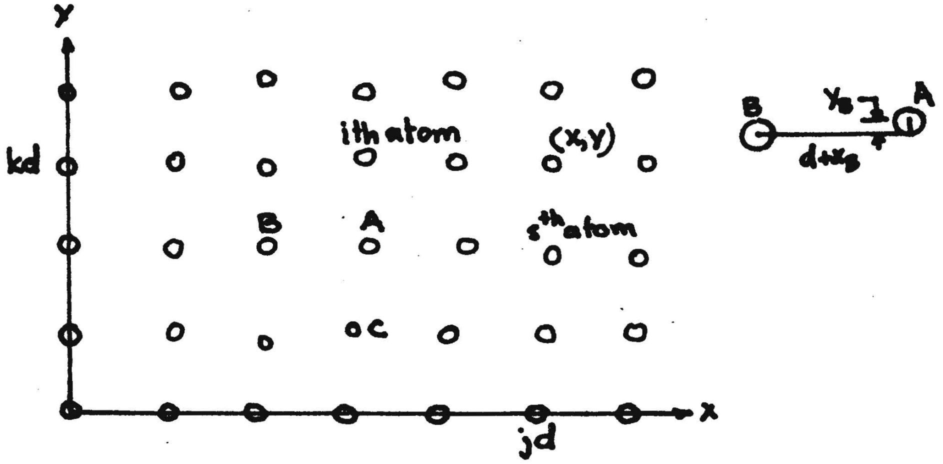

Fig. 5.

energy gained by an atom be determined by its relative displacements with respect to the two neighbouring atoms, one to the left and one towards the bottom, the atoms lying on the reference axes being constrained to move along the axes thus serving as reference lines relative to which all displacements can be measured. With this arrangement all the l links are taken care of and we are ready to proceed with the determination of the potential energy functions.

Let the displacement of the atom A relative to B be $d+x_B, y_B$, and let its displacement relative to C be $x_C, d+y_C$, the potential energy due to the disfigurement of the AB link will then be given by, assuming Hooke's law to be valid in the range of displacement,

$$W_B = \exp.\left[-\frac{K}{2kT}\left\{\sqrt{(d+x_B)^2+y_B^2}-d\right\}^2\right]$$

$$\left\{\sqrt{(d+x_B)^2+y_B^2}-d\right\}^2 = (d+x_B)^2+y_B^2+d^2-2d\sqrt{(d+x_B)^2+y_B^2}$$

$$= 2d^2+2dx_B+x_B^2+y_B^2-2d(d+x_B)$$

$$\doteq 2d^2+x_B^2+y_B^2+2dx_B-2d(d+x_B)$$

$$= x_B^2+y_B^2-y_B^2d/(d+x_B) + y_B^4d/4(d+x_B)^3 \doteq x_B^2$$

$$\therefore W_B \doteq e^{-\beta x_B^2}, \text{ where } \beta = \frac{K}{2kT}$$

Similarly it can be proved that $W_C \doteq e^{-\beta y_C^2}$

The partition function will then be given by,

$$z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^N \int\int\cdots\int e^{-\frac{W_0}{kT}} e^{-\beta\left(\sum_{i=1}^N x_i^2 + \sum_{i=1}^N y_i^2\right)} dx_i\,dy_i \int_{N\sigma^2}^{A} da$$

subject to $a - Nd^2 = d(\sum_{i=1}^N x_i + \sum_{i=1}^N y_i)$, where a is the area of the lattice, N is the total number of atoms, and W_0 is the static potential. Proceeding the same way as with the one-dimensional case, the partition function becomes:

$$z = e^{-\frac{W_0}{kT}}\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^N\left(\frac{\pi}{\beta}\right)^N\frac{1}{2}\left[\operatorname{erf}\sqrt{\frac{\beta}{2Nd^2}}(A-Nd^2)+\operatorname{erf}\sqrt{\frac{\beta}{2Nd^2}}N(d^2-\sigma^2)\right]$$

The various thermodynamic expressions are:

$$P = kT\sqrt{\frac{\beta}{2Nd^2}}\;\frac{\operatorname{erf}'\sqrt{\frac{\beta}{2Nd^2}}(A-Nd^2)}{\operatorname{erf}\sqrt{\frac{\beta}{2Nd^2}}(A-Nd^2)+\operatorname{erf}\sqrt{\frac{\beta}{2Nd^2}}(Nd^2-N\sigma^2)}$$

$$\Delta S = (W_{0s} - W_{0l})/T + Nk \ln (\rho_s/\rho_l)$$

$$C_v = 2Nk$$

The distribution functions can can be derived as below:

Let the equilibrium position of an atom be (jd,kd). Then the probability of finding the atom at (x,y) will be

$$P_{j,k}(x,y) = \left(\frac{\beta}{\pi}\right)^N \iint \cdots \int e^{-\beta\left(\sum_{i=1}^{j} x_i^2 + \sum_{s=1}^{k} y_s^2\right)} dx_i \, dy_s$$

subject to $x - jd = \sum_{i=1}^{j} x_i$, $y - kd = \sum_{s=1}^{k} y_s$, where x_i is the displacement from equilibrium position of the ith atom from (i-1)th atom in the kth horizontal chain, and y is the displacement from equilibrium position of the sth atom from (s-1)th atom in the jth vertical chain (Fig. 5).

Proceeding similarly as before,

$$P_{j,k}(x,y) = \frac{\beta}{\pi} \frac{1}{\sqrt{j}} e^{-\frac{\beta}{j}(x-jd)^2} \frac{1}{\sqrt{k}} e^{-\frac{\beta}{k}(y-kd)^2}$$

Thus in our simplified model of the square lattice the atoms vibrate the same way as if the lattice was made of independent linear chains superposed together.

THREE-DIMENSIONAL MODEL

The partition function for a three-dimensional model can be set up the same way as that for the two-dimensional model. For a simple cubic lattice this becomes,

$$z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \iint \cdots \int e^{-\frac{W_0}{kT}} e^{-\beta\left(\sum_i x_i^2 + \sum_i y_i^2 + \sum_i z_i^2\right)} dx_i dy_i dz_i \int_{N\sigma^3}^{V} dv$$

subject to $v - Nd^3 = d^2\left(\sum_{i=1}^{N} x_i + \sum_{i=1}^{N} y_i + \sum_{i=1}^{N} z_i\right)$, the final form being,

$$z = e^{-\frac{W_0}{kT}} \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \left(\frac{\pi}{\beta}\right)^{\frac{3N}{2}} \frac{1}{2}\left[\operatorname{erf} \sqrt{\frac{\beta}{3Nd^4}}(V - Nd^3) + \operatorname{erf} \sqrt{\frac{\beta}{3Nd^4}} N(d^3 - \sigma^3)\right]$$

$$P = kT\sqrt{\frac{\beta}{3Nd^4}} \frac{\operatorname{erf}' \sqrt{\frac{\beta}{3Nd^4}}(V - Nd^3)}{\operatorname{erf} \sqrt{\frac{\beta}{3Nd^4}}(V - Nd^3) + \operatorname{erf} \sqrt{\frac{\beta}{3Nd^4}} N(d^3 - \sigma^3)}$$

$$C_v = 3Nk$$

$$\Delta S = (W_{0s} - W_{0l})/T + (3/2)Nk \ln(\beta_s/\beta_l)$$

$$P_{h,k,l}(x,y,z) = \left(\frac{\beta}{\pi}\right)^{3/2} \frac{1}{\sqrt{h}} e^{-\frac{\beta}{h}(x-hd)^2} \frac{1}{\sqrt{k}} e^{-\frac{\beta}{k}(y-kd)^2} \frac{1}{\sqrt{l}} e^{-\frac{\beta}{l}(z-ld)^2}$$

The mean quadratic fluctuation of any atom relative to any other "reference atom" due to heat motion will be given by $\overline{\xi^2_{h,k,l}} = \overline{(R - \bar{R})^2}$, where R is the distance of the atom, whose equilibrium position with respect to the reference atom is (hd, kd, ld), from the reference atom at any time and $\bar{R}$ is the mean distance equal to $d\sqrt{(l^2 + k^2 + h^2)}$. If the position vector of the moving atom from its equilibrium position be denoted by $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$, and if its projection on the line joining the reference atom and the equilibrium position of the moving atom be $\vec{r}_p$, then, since $|\vec{r}|$ is small compared to R, $(R - \bar{R})$ can approximately be taken to be equal to $|\vec{r}_p|$.

$$\therefore \overline{\xi^2_{h,k,l}} = \overline{|\vec{r}_p|^2} = \overline{x_p^2 + y_p^2 + z_p^2}$$

= sum of the projections of the mean square fluctuations in the three co-ordinate directions

$$= \frac{1}{2\pi}\frac{\pi}{\beta}\left[h\frac{h}{\sqrt{(h^2+k^2+l^2)}} + k\frac{k}{\sqrt{(h^2+k^2+l^2)}} + l\frac{l}{\sqrt{(h^2+k^2+l^2)}}\right]$$

$$= \frac{1}{2\beta}\sqrt{(h^2+k^2+l^2)}$$

Thus the relative distribution function can be written as

$$\rho(r) = \sqrt{\frac{\beta}{\pi}}\frac{1}{4\pi r^2}\sum_s \frac{n_s}{\sqrt{(\bar{R}_s/d)}}e^{-\frac{\beta d}{\bar{R}_s}(R-\bar{R}_s)^2}$$

where n_s is the number of atoms at a mean distance of $\bar{R}_s$ from the reference atom.

The structure diffusion constant can accordingly be defined as

$$D = \frac{\overline{\xi_s^2}}{2\bar{R}_s} = \frac{1}{4d\beta}$$

X-RAY SCATTERING

The pattern of x-ray scattering is very closely related to the relative distribution function. The intensity distribution of the rays scattered by an isotropic system of like atoms has been derived by Zernicke and Prins,(26) giving

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(26) Zernicke and Prins, Z. f. Phys., 41 (1927) 184.

$$\frac{1}{8\pi\rho_0}(E-1)k = \int_0^\infty \left(\frac{\rho(r)}{\rho_0} - 1\right) r \sin(kr)\,dr$$

where E is the relative intensity of the scattered rays, ρ_0 is the value of $\rho(r)$ when $r \to \infty$, and $k = \frac{4\pi}{\lambda}\sin\frac{1}{2}\theta$, where λ is the incident wavelength and θ is the angle of scattering. This formula can be regarded as an expansion into Fourier integral of the quantity $(E-1)k/8\pi\rho_0$ as a function of the parameter k, with the factor $\rho/\rho_0 - 1$ acting as the corresponding Fourier amplitude. This factor can accordingly be determined from the experimental data, referring to the function E(k) with the help of the Fourier transformation

$$\left(\frac{\rho}{\rho_0} - 1\right) r = \frac{1}{8\pi\rho_0} \int_0^\infty (E-1)k \sin(kr)\,dk$$

The results obtained by applying this formula to a number of simple liquids are in fair agreement with the derived $\rho(r)$,(27) where the broadening is increased as the square root of the mean radius of the layers of atoms, and it is conjectured that the same formula for $\rho(r)$ will apply to polycrystalline solid.

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(27) Frenkel, J., op. cit., p. 118.

CONCLUSION

The thermodynamic and structural properties of simple models of solids and liquids can be derived, with the help of an artifice, on the basis of a Gaussian-type distribution function and employing Boltzmann statistics to a fair degree of accuracy. This does not call for the mathematical complications of the more exact theories, nor the artificiality of the simpler, but rather idealistic models. The final results depend on two physical parameters: the static potential when all the atoms are at equilibrium in the lattice, and the frequency of heat motion of the atoms.

The solid and the liquid states near the melting point of a substance can be regarded as having essentially the same structure, but with different structural constants. The varying degrees of order in the two phases can be attributed to the atomic frequencies of heat motion and temperature. From this stand point the distant order in solids is nothing but a large local order. The "migration-diffusion" of structure and the corresponding entropy term can be neglected compared to the diffusion due to vibration.

SUMMARY

The thermodynamic and structural properties of solids and liquids have been studied on the basis of simple linear models, using a Gaussian distribution function and Boltzmann statistics. With the help of an artifice, the one-dimensional partition function, equation of state, change in entropy on fusion, specific heat, relative distribution function, and the structure diffusion constant have been derived, and an attempt has been made to extend the one-dimensional model to two- and three-dimensional cases. Also the notion of distant and local orders has been discussed from a new angle.

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