

Kirkwood's equation,¹² which is also based on (59), does not negate this opinion, because it only diverges at high densities which could be interpreted in different ways.

Mathematical modelings or the approximations which are done for solid state, or are based on consideration of the ordered orientations of the molecules in the system, are more likely to be able to predict

the liquid-solid phase transition. This matter will be considered in a forthcoming paper.

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Variational Approach to Melting. II*

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A variational approach to the equilibrium thermodynamic properties of an original system based upon an inequality for the Helmholtz free energy of that system is introduced. A system with molecules obeying the cell model of Lennard-Jones and Devonshire, and having a harmonic-oscillator-type potential function inside their cells, is used for a reference system to produce the inequality for the Helmholtz free energy of the original system. Optimization upon this inequality indicates that a variational calculation based on a reference system with highly ordered structure, as the cell model, predicts the properties of the solid phase better than the liquid phase. Also, it shows that by an ordered-structure reference model, it is possible to predict the liquid-solid phase transition. Equilibrium thermodynamic properties of the solid phase and liquid-solid phase equilibria are calculated and are compared with the machine-calculated and the experimental data.

I. INTRODUCTION

The solid-liquid phase transition is probably one of the first phenomena to be observed by man, while it remains among those least well understood by him. This is not entirely due to a lack of effort since a large number of approaches have been proposed to account for melting. The early approaches were largely semi-empirical in nature. The two best known melting equations resulting from this effort are the Lindemann equation¹ and the Simon equation.² In addition, a number of other approaches to melting have been based upon the assumption that melting is the result of the solid's becoming unstable for some reason or another.³ Lennard-Jones and Devonshire⁴ proposed a model in which melting is treated as an order-disorder transition. This approach contains one free constant which is fixed by fitting to the triple-point melting temperature.

The above-mentioned approaches have not been en-

tirely satisfactory. The most likely reason for their failure is that they either disregard the properties of the liquid entirely, or else treat them in a manner which is quite inadequate. An attempt to include the liquid as an equal partner in the solid-liquid transition resulted in the theory of Kirkwood and Monroe.⁵ This approach is formally exact, but a number of approximations must be made in order to obtain numerical results which are not very satisfactory.

In the present work a variational approach to the melting and the equation of state of solids is proposed. An inequality based on a cell model reference system for the Helmholtz free energy is produced, and by the variational calculation upon this inequality the equilibrium thermodynamic properties of melting and solid are calculated.

II. THE BASIC INEQUALITY AND THE REFERENCE SYSTEM

It was shown⁶ in I that for the ratio of the Helmholtz free energies of two different systems, the following inequality holds:

$$F \leq F_0 + \langle U - U_0 \rangle_0, \quad (1)$$

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¹ P. A. Lindemann, *Physik. Z.* **11**, 609 (1910).

² L. Slater, *Phil. Mag.* **45**, 369 (1954). See also J. J. Gilvarry, *Phys. Rev.* **102**, 308, 317, 325, 331 (1956).

³ K. F. Hertzfeld and M. Goepfert-Mayer, *Phys. Rev.* **46**, 995 (1934). See also M. Born, *J. Chem. Phys.* **17**, 591 (1939).

⁴ J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* **A170**, 464 (1939).

⁵ J. G. Kirkwood and E. Monroe, *J. Chem. Phys.* **9**, 514 (1941). See also R. Brout, *Physica* **29**, 1041 (1963).

⁶ G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.* **51**, 4958 (1969). This paper will be referred to as I.

and by introducing the partition functions, we get

$$Q/Q_0 \geq \exp[\langle -\beta(U - U_0) \rangle_0], \quad (2)$$

where Q_0 , F_0 , and U_0 are partition function, Helmholtz free energy, and total potential energy of a reference system while Q , F , and U are properties of the original system. The angled brackets mean the expectation values over the reference system. As was mentioned in I, the more nearly the reference system approximates the original system, the more nearly the above inequality is to an equality.

The formulation in I was based upon the assumption that the original system is a fluid (liquid or gas). On this basis, the reference system was taken as a fluid consisting of particles having only hard-core potential [because in the derivation of the Percus-Yevick equation, it was assumed that $g(\mathbf{r}) = g(|\mathbf{r}|)$ which is only correct for fluids]. In this part of the work, we are going to find the properties of the original system in solid phase. For this purpose, it is necessary to choose a reference system which resembles a solid phase. In other words, we choose a reference system with correlation functions which are dependent not only on the intermolecular distances, but also the orientation of the molecules with respect to each other in the system. For this purpose, the cell model of Lennard-Jones and Devonshire,⁷ will be used as the reference system. As the works of many investigators have shown⁸ the cell model of Lennard-Jones and Devonshire,^{7,9} which was originally designed to predict the liquid state is actually a model for the solid state. According to cell theory, the potential energy of the system can be approximated by a sum of terms each depending on the position of just one molecule. If this were not so, the force on one molecule would depend on the position of another and the motions of the molecules would not be independent. Thus, it is assumed that

$$U_0 = \Phi_0 + \sum [\Psi(\mathbf{r}_i) - \Psi(0)], \quad (3)$$

where \mathbf{r}_i is the vector displacement of molecule i from the center of its cell and Φ_0 is the potential energy when all molecules are at their cell centers. It is clear from (3) that $[\Psi(\mathbf{r}_i) - \Psi(0)]$ is the change of potential energy when the molecule i moves from its cell center to the point \mathbf{r}_i , with all other molecules remaining at their cell centers. With the potential energy approximated by (3), the configuration integral is given by

$$Q(N, V, T) = \exp(-\Phi_0/kT) v_f^N. \quad (4)$$

The "free volume" v_f is defined by

$$v_f = \int_{\Delta} \exp\left(-\frac{\Psi(\mathbf{r}_i) - \Psi(0)}{kT}\right) d\mathbf{r}_i. \quad (5)$$

The integration in (5) is to be taken throughout the interior of the cell. If we consider the lattice of cell centers as a face-centered cubic (fcc) lattice, the most obvious choice for the cell shape will be then dodecahedron. If we replace the dodecahedrons by spheres of diameter a_0 and consider the "smearing approximation," as introduced by Lennard-Jones and Devonshire,⁹ which is quite accurate particularly at high densities, we get from (5)

$$v_f = 4\pi a_0^3 G = 4\sqrt{2}\pi(V/N)G, \\ G = \int_0^{0.5} x^2 \exp\left(-\frac{\Psi(\mathbf{r}) - \Psi(0)}{kT}\right) dx, \quad (6)$$

because for face-centered cube crystal structure

$$a_0 = (\sqrt{2}N/V)^{1/3}. \quad (7)$$

If we define the potential of each atom in its cell, relative to the center, as $W(\mathbf{r})$, then

$$W(\mathbf{r}) = \Psi(\mathbf{r}) - \Psi(0). \quad (8)$$

The average value of potential of each atom in its cell is

$$\langle \Psi(\mathbf{r}) \rangle_{\Delta} = \langle W(\mathbf{r}) \rangle_{\Delta} + (\Phi_0/N) \quad (9)$$

where $\Phi_0/N = \Psi(0)$ and the averages are over cells such that

$$\langle \chi \rangle_{\Delta} = \int_{\Delta} \chi P(\mathbf{r}) d\mathbf{r}, \quad (10)$$

and

$$P(\mathbf{r}) d\mathbf{r} \\ = \left[\exp\left(-\frac{W(\mathbf{r})}{kT}\right) d\mathbf{r} \right] / \left[\int_{\Delta} \exp\left(-\frac{W(\mathbf{r})}{kT}\right) d\mathbf{r} \right], \quad (11)$$

where χ could be any variable in the cell, and $P(\mathbf{r}) d\mathbf{r}$ is the probability that a given molecule is at a distance between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ from the center of its cell.

The radial distribution function in a system following the cell theory of Lennard-Jones and Devonshire¹⁰ as explained above is

$$g(r) = \frac{1}{16\pi} \sum_i \frac{N_i}{Z_i r} \int_{|y-a_i|}^{(1/2)a_0} \frac{P(R') dR'}{R'} \int_{|y-r|}^{(1/2)a_0} \frac{P(R) dR}{R}, \quad (12)$$

where N_i is the number of neighbors with i th shell and Z_i is the distance of the i th neighbors from the central molecules, $Z_i = a_0$; the summation in (12) is over the shells of the neighbors.

If the cell field, $W(\mathbf{r}) = \Psi(\mathbf{r}) - \Psi(0)$, is considered to be a harmonic field, that is,

$$W(\mathbf{r}) = kT(\mathbf{r}/a_0)^2 A \quad (13)$$

⁷ J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A163**, 53 (1937).

⁸ J. A. Barker, *Lattice Theories of Liquid State* (Pergamon Press Inc., New York, 1963).

⁹ J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A165**, 1 (1938).

¹⁰ J. Corner and J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A178**, 401 (1941).

the relations for free volume, average potential, and radial distribution function can be evaluated analytically.¹⁰ For this, it is also necessary to assume that the potential rises so steeply that the particle is effectively confined to a cell. This is like neglecting quantities involving $\exp(-\frac{1}{4}A)$, and this is only possible when the value of A is very large. In the later sections of this work, we will see that the values of A which are produced by variational calculations are so large that this is not any more an assumption or approximation but a reality.

Inserting relation (13) in (6), for very large values of A , we get

$$G = \int_0^\infty x^2 \exp(-Ax^2) dx = \sqrt{\pi} A^{-3/2}. \quad (14)$$

Then

$$v_f = (2\pi^3)^{1/2} (V/N) A^{-3/2}$$

and Helmholtz free energy, $F = -kT \ln Q$,

$$F_0 = \Phi_0 + NkT [\ln \rho + \frac{3}{2} \ln A - \frac{1}{2} \ln(2\pi^3)]. \quad (15)$$

Also, from relations (10) and (13) again, considering A very large, we can write

$$\begin{aligned} \langle W(\mathbf{r}) \rangle_\Delta &= \int_0^\infty x^4 \exp(-Ax^2) (AkT) dx / \int_0^\infty x^2 \exp(-Ax^2) dx \\ &= \frac{3}{2} kT. \quad (16) \end{aligned}$$

Then from relations (16) and (9) we get for the average value of the potential energy of each atom the following relation:

$$\langle \Psi(\mathbf{r}) \rangle_\Delta = \frac{3}{2} kT + (\Phi_0/N), \quad (17)$$

which is the classical value for the average potential energy of each atom.

For the radial distribution function, by considering harmonic field, Corner and Lennard-Jones¹⁰ have shown that the relation (12) takes the following form:

$$g(r) = \frac{A^{1/2}}{4\sqrt{2}\pi^{3/2}\rho a_0} \sum_i \frac{N_i}{Z_i} r^{-1} \exp\left[-\frac{1}{2}A \left(\frac{Z_i-r}{a_0}\right)^2\right], \quad (18)$$

with the following constraint for the contribution of each shell of neighbors:

$$Z_i - a_0 < r < Z_i + a_0. \quad (19)$$

III. THE BASIC INEQUALITY IN THE CASE OF SOLID PHASE

In the case of solid phase, the cell model with harmonic field as expressed above is taken as the reference system. With the original system following Lennard-Jones potential function, the total potential of the original system is:

$$U = \sum_{i>j=1}^N u(\mathbf{r}_{ij}), \quad (20)$$

and with the reference system following the cell model as expressed above the total potential of the reference system is:

$$U_0 = \sum_{i=1}^N \Psi(\mathbf{r}_i). \quad (21)$$

The summation in relation (20) is over the intermolecular distances, while the summation in (21) is over the cells. By inserting relations (20) and (21) in inequality (2), we get

$$F \leq F_0 + 2\pi N \rho \int_0^\infty u(r) g_0(r) r^2 dr - N \langle \Psi(\mathbf{r}) \rangle_\Delta. \quad (22)$$

By using F_0 as given by (15), replacing $g_0(r)$ by $g(r)$ as given by (18) and considering the constraints (19), by replacing $\langle \Psi(\mathbf{r}) \rangle_\Delta$ by its value as given by (17), and by using the Lennard-Jones 12:6 potential for the original system, inequality (22) takes the following form:

$$\begin{aligned} F \leq NkT [\ln \rho + \frac{3}{2} \ln A - \frac{1}{2} \ln(2\pi^3)] - \frac{3}{2} NkT \\ + 2\pi N \rho \frac{A^{1/2}}{4\sqrt{2}\pi^{3/2}\rho a_0} \sum_i \frac{N_i}{Z_i} \int_{\alpha_i}^{\beta_i} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] r \\ \times \exp\left[-\frac{1}{2}A \left(\frac{Z_i-r}{a_0}\right)^2\right] dr, \quad (23) \end{aligned}$$

where

$$\begin{aligned} \alpha_i &> Z_i - a_0, \\ \beta_i &< Z_i + a_0, \end{aligned}$$

for every term of the summation which is related to each shell of neighbors.

As was shown before, for fcc crystal structure one has $a_0 = (\sqrt{2}/\rho)^{1/3}$, where a_0 is the diameter of the smeared cell, and ρ is the number density. Now if we introduce all the variables in dimensionless forms as follows:

$$\begin{aligned} a_0^* &= a_0/\sigma = (\sqrt{2}/\rho^*)^{1/3}; & \rho^* &= \rho\sigma^3, \\ x &= r/\sigma, \\ Z_i^* &= Z_i/a_0, \end{aligned}$$

and the dimensionless temperature

$$T^* = kT/\epsilon,$$

then inequality (23) takes the following form:

$$\begin{aligned} \frac{F}{NkT} \leq \ln(\rho A^{3/2}) \\ + (T^* a_0^{*2})^{-1} \left[\frac{2A}{\pi} \right]^{1/2} \sum_i \frac{N_i}{Z_i^*} \int_{\alpha_i^*}^{\beta_i^*} \left[\frac{1}{x^{12}} - \frac{1}{x^6} \right] x \\ \times \exp\left[-\frac{1}{2}A (Z_i^* - x/a_0^*)^2\right] dx - \frac{3}{2} - \frac{1}{2} \ln(2\pi^3), \quad (24) \end{aligned}$$

where

$$\begin{aligned} \alpha_i^* &> (Z_i^* - 1) a_0^*, \\ \beta_i^* &< (Z_i^* + 1) a_0^*. \end{aligned}$$

and

Inequality (24) is the basic inequality which will be dealt with in calculating the properties of the solid phase.

IV. CHOICE OF THE PROPER NUMBER OF SHELLS OF NEIGHBORS

In inequality (24) the summation sign is over the shells of the neighbors of a central molecule. This summation actually is for $i=1 \rightarrow \infty$, as an infinite series. This series will be convergent if the terms of the series follow the convergent criteria of the infinite series. As was mentioned above, Lennard-Jones and Devonshire considered the "smearing approximation" for deriving the cell theory relations as given before. This smearing approximation could only be close to reality when there are enough particles in every shell such that it be possible to claim the potential inside every shell is angle independent. But actually, for any kind of crystal structure (including fcc crystal), this is not the case. In other words, the number of molecules does not increase rapidly enough as the shell size increases to maintain the validity of the smearing approximation (see Ref. 11). To maintain the validity of the smearing approximation, it will be important to use the minimum number of shells. For this purpose, we must find the smallest number of shells that can be used while not disturbing the sign of the inequality and the functional form of the variables involved. For Lennard-Jones 12:6 potential, which is considered for the original system,

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

we have

$$u(r) > 0 \quad \text{for } (r < \sigma),$$

$$u(r) < 0 \quad \text{for } (r > \sigma).$$

With the fact that $g_0(r)$, the radial distribution function, is always positive or zero, inequality (22) could be written as

$$F \geq F_0 + 2\pi N \rho \int_0^\theta u(r) g_0(r) r^2 dr - N \langle \Psi(\mathbf{r}) \rangle_\Delta \quad (25)$$

for $\theta > \sigma$. This is because the contribution to the integral in inequality (25) for $r > \theta$ is always negative. Similarly, inequality (24) remains valid for

$$\alpha_i^* > 1,$$

or it is enough to have

$$(Z_i^* - 1)(\sqrt{2}/\rho^*)^{1/2} \geq 1 \quad (26)$$

to keep the inequality still valid, while the minimum number of the shell neighbors are used. Then condition (26) is for the first of the shells which we can disregard. Since for a fcc crystal $Z_i^* = i^{1/2}$; $i = 1, 2, 3, \dots$, then we must have for i , the index of the first of the

shells to disregard,

$$i^{1/2} - 1 \geq (\rho^*/\sqrt{2})^{1/2}.$$

The largest value of ρ^* is the close-packed density, $\rho^* = \sqrt{2}$, then in the extreme case

$$i^{1/2} - 1 \geq 1 \quad \text{or } i \geq 4.$$

Then we can disregard the 4th, 5th, 6th, \dots shells. Consequently, if we consider only the first three shells, not only the sign of the inequality will not be disturbed, but the effect on the validity of the smearing approximation will be the least possible.

V. CHOICE OF THE VARIATIONAL PARAMETER

With the consideration of only the first three shells, we have

$$F/NkT \leq \ln(\rho A^{3/2}) + (T^* a_0^{*2})^{-1} [2A/\pi]^{1/2} \\ \times \sum_{i=1}^3 \frac{N_i}{Z_i^*} \int_{\alpha_i^*}^{\beta_i^*} \left[\frac{1}{x^{12}} - \frac{1}{x^6} \right] x \\ \times \exp\left[-\frac{1}{2}A(Z_i^* - x/a_0^*)^2\right] dx - \frac{3}{2} - \frac{1}{2} \ln(2\pi^3), \quad (27)$$

with

$$\alpha_i^* > (Z_i^* - 1)a_0^*; \quad \beta_i^* < (Z_i^* + 1)a_0^* \quad (28)$$

where for fcc crystal¹¹

i	Z_i^*	N_i
1	1	12
2	$\sqrt{2}$	6
3	$\sqrt{3}$	24.

The only variable in the right-hand side of the inequality (27) which does not appear in the left-hand side of the inequality is A . A is proportional to the square of the frequency of the oscillation of the molecules in their cells. With a similar argument as given in I, A could be considered as the variational parameter for the minimization of the right-hand side of the inequality (27).

VI. RESULTS

Inequality (27) with conditions (28) for α_i^* and β_i^* is the working inequality for the Helmholtz free energy. Minimization of the right-hand side of the inequality (27) should be performed with respect to A . Numerical calculations by electronic computer shows that the right-hand side of inequality (27) has always only one relative minimum with respect to A for every temperature T^* and density ρ^* which was investigated.

The Helmholtz free energy, which is a result of the variational calculation on the right-hand side of (27), is supposed to be more satisfactory for the solid state than for the fluid state. This is because the reference system which is chosen to produce the inequality (27) more nearly resembles a solid system.

Figure 1 shows the values of A which are calculated

¹¹ J. A. Prins and H. Peterson, *Physica* **3**, 147 (1936).

for a range of densities for four different isotherms. The values of A are always large which support the accuracy of relations (14), (16), and (18) for which the values of A , *a priori*, were assumed to be large.

Figure 2 indicates the compressibility of the solid phase of a system of molecules following Lennard-Jones 12:6 potential function. The compressibility is calculated from the Helmholtz free energy, which is a result of the variational calculation of inequality (27), and

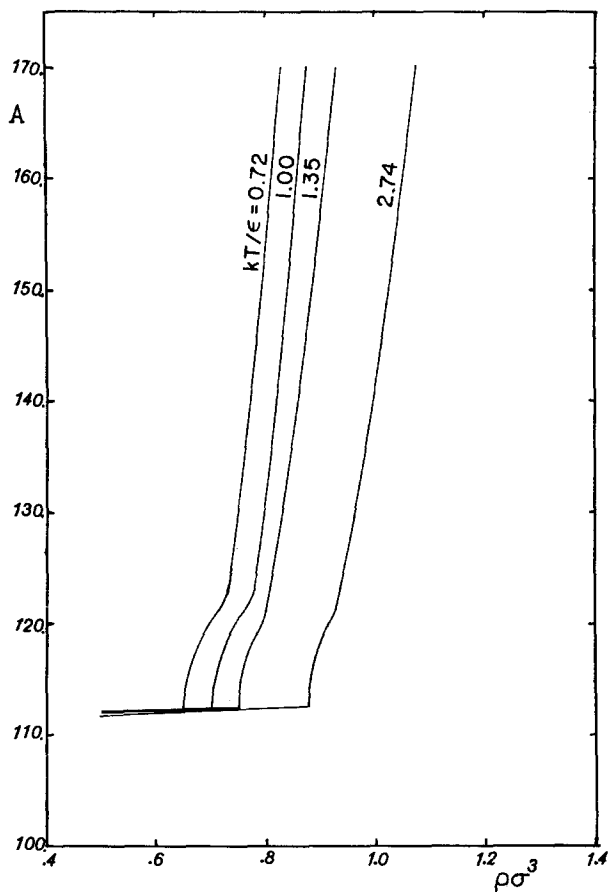


FIG. 1. Values of A vs density for different isotherms as calculated by the variational calculations. $A = m\omega^2(kT)$, where ω is the frequency of oscillation of the molecules of the reference system in their cells and m is the particle's mass.

thermodynamic relation

$$PV/NkT = \rho(\partial/\partial\rho)(F/NkT)_{T,N_i}$$

The compressibilities which are calculated by the present variational calculation for Lennard-Jones solid are compared with machine-calculated data on Fig. 2. As is clear in this figure, the compressibility has a discontinuity at a particular density for every isotherm. These discontinuities are related to the sharp changes of slopes of A for each isotherm on Fig. 1. The discontinuities in the isotherms on Fig. 2 are clear indications of solid-liquid phase transitions. Even though inequality (27) still has solutions for densities less

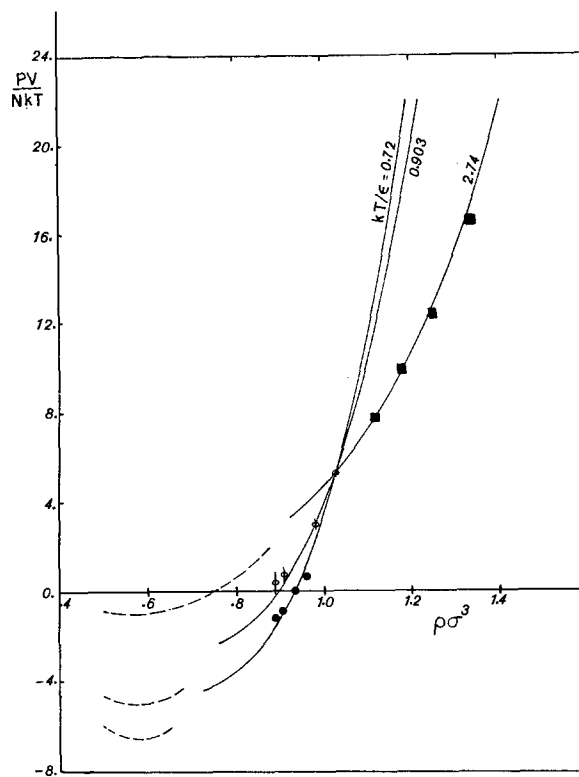


FIG. 2. Equation of state of Lennard-Jones 12:6 solid for different isotherms. The points shown by ϕ , \bullet , and \blacksquare are machine-calculated values for solid phase [D. Henderson and J. A. Barker, *Mol. Phys.* **14**, 587 (1968); I. P. Bazarov, *Sov. Phys.—Dokl.* **135**, 1293 (1960); M. Ross and B. J. Alder, *Phys. Rev. Letters* **16**, 24, 1077 (1966)].

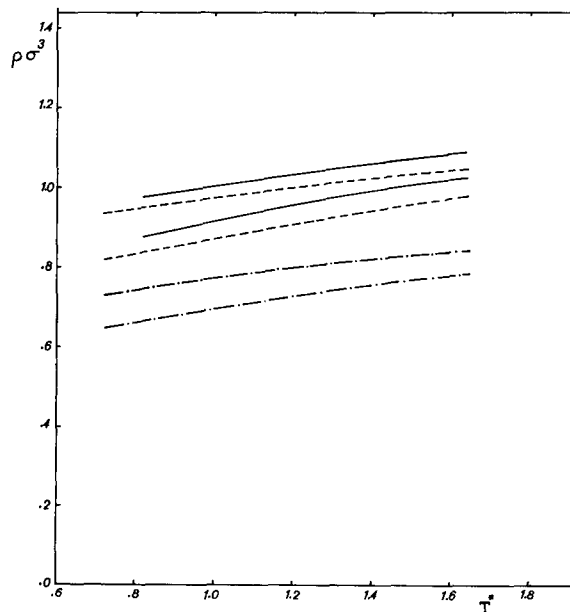


FIG. 3. Densities of coexisting liquid and solid phases vs temperature. The solid lines are the experimental values for argon [I. R. McDonald and K. Singer, *Discussions Faraday Soc.* **43**, 40 (1967)]. The dashed lines are calculated from the system of Eqs. (29). The dot-dashed lines are the values related to the sharp changes of the slope of A vs $\rho\sigma^3$ for different isotherms in Fig. 1.

than the solid-liquid phase transition densities, the resulting values for Helmholtz free energy and other thermodynamic properties are not expected to be correct. This is because the reference system on which the inequality (27) is based resembles a solid phase. In fact, comparison with machine-calculated data proves this argument. (Compare Fig. 3 of I and Fig. 2 of the present paper.) Figure 3 shows the coexisting phase densities of the two liquid and solid phases versus temperature. There are two ways to calculate the coexisting phase data. The first method is the predictive way which was discussed above and which is based upon the breaks of the compressibility curves or the sharp changes of the slopes on the graphs of A versus density for different isotherms as shown in Fig. 1. The second method is by solving the following system of two equations:

$$\begin{aligned}(F+PV)_l &= (F+PV)_s, \\ P_l &= P_s,\end{aligned}\quad (29)$$

for ρ^* and ρ_s^* . This system of two equations and two unknowns are solved graphically as was explained in I for the liquid-vapor equilibria calculations. In these graphical calculations, the values of $(F+PV)_l$ and P_l calculated from Eq. (52) of I are used. In Fig. 3, the results of the above two methods are compared with the coexisting liquid-solid experimental data of argon. Figure 3 indicates that the second method, based upon the solution of Eq. (29), gives much better results than the first method. While the result of the first method quantitatively is not of significance, its predictive character of the solid-liquid phase transition is of importance. A similar approach, like the second method which is introduced above, is used by Henderson and Barker¹² for the melting transition of argon.

VII. DISCUSSION

The above results indicate that a variational calculation based upon an ordered-structure reference system which resembles more a solid phase than a liquid is able to predict the liquid-solid phase transition. However, a more flexible reference system would be expected to yield better predictions of the thermodynamic properties of both phases and of the liquid-solid phase transition.

¹² W. W. Wood and F. R. Parker, *J. Chem. Phys.* **27**, 720 (1957).

A similar, but more elementary, variational calculation for the prediction of the melting point of simple solids has been proposed by Bazarov.¹³ The basic inequality which is used by Bazarov for the Helmholtz free energy of the system is in accordance with the Bogolyobov variational principle which is unfamiliar to these authors. According to this principle, the free energy of a crystal structure is determined from the expression

$$F \leq F_0 + \langle U_1 \rangle_0, \quad (30)$$

where F is the free energy of the crystal, F_0 is the free energy corresponding to the energy U_0 , and $\langle U_1 \rangle_0$ is the value of the energy $U_1 = U - U_0$ averaged over U_0 . Bazarov does not give any explanation for the mathematical significance or the physical meaning of F_0 and U_0 . While inequality (30) is apparently similar to the basic inequality (2) which is used in the present variational calculations, it seems to have less significance. This is because inequality (30), as Bazarov implies, holds only for crystals while inequality (2) holds for any state of the matter, in equilibrium conditions. Bazarov does not show how well his inequality for the Helmholtz free energy of the crystals predicts the thermodynamic properties of solids. But he indicates that the ratio of the melting point predicted by his method and the experimental melting point of simple substances (Ar, Ne, Kr, and Xe) is exactly the same and is approximately equal to three. For the present method also, this ratio is approximately equal to 3 for the predictive approach which was related to the sharp change of slope of A versus ρ^* on Fig. 1. But if the second approach which was based on the solution of Eq. (29) is used, this ratio will be approximately equal to 1.3 which is much closer to unity. It is expected that if a reference system with more freedom for randomness of the relative positions of the molecules than the cell model is used, the liquid-solid phase transition could be predicted more accurately.

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¹³ R. K. Crawford, thesis, Princeton University, 1968; see also, R. K. Crawford and W. B. Daniels, *Phys. Rev. Letters* **21**, 363 (1968).