PHYSICAL REVIEW A VOLUME 15, NUMBER 3 MARCH 1977

Vacancy theory of melting and condensation*

D. E. O'Reilly
Argonne National Laboratory, Argonne, Illinois 60439

(Received 7 September 1976; revised manuscript received 29 November 1976)

A cell model in which the cell size is constant at fixed temperature and pressure is utilized to calculate melting data and gas-liquid critical constants. Interactions between vacancies are taken into account and the variation of vibrational free energy with vacancy concentration is incorporated into the model. The calculated results agree well with experiment for the hard-sphere transition and melting and condensation of argon. The pair correlation function for argon computed from the model is in good agreement with experiment with reasonable values of the parameters in the calculation. The calculations indicate that vacancy defects exist in liquids and play an essential role in determining melting conditions.

I. INTRODUCTION

The existence of molecular vacancy defects in the solid state is well established, and there is considerable evidence at the present time to indicate that vacancies exist in liquids but with a much higher concentration than in solids. The most direct information concerning vacancies in fluids may be found in machine calculations on Lennard-Jones atoms confined to a two-dimensional plane.[1] In the "snapshots" of the instantaneous configuration of the model fluid, holes of atomic dimension are clearly seen. These holes persist in time and migrate as the particles move. From the trajectories of the particles in the model fluid it is apparent that the atoms "rattle" about an equilibrium position and migrate towards the holes if a hole is adjacent to a "rattling" site.

In the results reported in Ref. 1, the vacancies do not appear to be randomly distributed, but rather tend to form clusters which become especially pronounced at the higher temperatures and lower densities given in Ref. 1. The position of the first maximum in the pair correlation function for computer argon[2] occurs at $r/\sigma = 1.09 \pm 0.01$ and the minimum in the Lennard-Jones pair potential energy $[V(r) = 4\epsilon_{LJ}\{(\sigma/r)^{12} - (\sigma/r)^6\}$, which was employed in the computer calculations] occurs at $r/\sigma = 2^{1/6} = 1.122$. The nearest-neighbor distance in solid argon at the melting point is equal[3] to 3.857 Å, and the maximum in the atomic density distribution function determined by x-ray and neutron diffraction[4] for the liquid at the melting point is 3.84 ± 0.07 Å. However, argon expands by 13% upon melting, and hence these facts imply that there are vacancies in the liquid.

The above results suggest that a cell-model approach to an understanding of the melting phenomenon might be useful. In the following we will adopt a cell model and choose the volume v_0 of the unit cell to be equal to the atomic volume as calculated from the density of the solid. Hence the center of essentially only one molecule can be contained in a given cell at a given time and a cell is either singly occupied or empty. Hence communal entropy effects are small except for hard spheres (Sec. V).

Recent evidence[5] for an ordered distribution of point defects in alkali halide crystals has been obtained. Some of the defects form a lattice and others are arranged in a partially ordered fashion.[5] These facts clearly indicate that one must consider interactions between defects, and in the following we do this for vacancies.

II. THEORY

A. Gibbs free energy function

As indicated in the Introduction, in the formulation of a theory of solids and fluids the interactions between vacancies must be taken into account. As will be shown later (Sec. II B) one may do this by an expansion of the internal energy U in powers of $\rho - \rho_0$, where ρ is the number density of the material and ρ_0 is the number density of the perfect solid at some reference (standard state) temperature (T_0) and pressure (P_0). That is

$$U(\rho, T_0, P_0) = U(\rho_0, T_0, P_0) + \left(\frac{\partial U}{\partial \rho}\right)_{T_0, P_0} (\rho - \rho_0) + \frac{1}{2}\left(\frac{\partial^2 U}{\partial \rho^2}\right)_{T_0, P_0} (\rho - \rho_0)^2 + \cdots \quad . \tag{1}$$

Let us now define a variable x which is the probability that a cell is empty; let the total number of molecules under consideration be N_0 and let N_0 be constant. The number of cells is N, the number of empty cells is N_v and $N = N_0/(1-x)$. Clearly $\rho = \rho_0(1-x)$ and hence Eq. (1) is an expansion of the internal energy in powers of x. To evaluate $(\partial U/\partial\rho)_{T_0,P_0}$ let us consider the perfect solid at the standard-state pressure P_0 and temperature T_0.

Now remove a molecule (molecule A) from a cell in the interior of the system and increase the number of cells by one where the new cell is on the surface of the sample. As shown in Appendix A the change in U for this process is $\Delta U = \epsilon/2$ (neglecting vibrational and relaxation effects) where $N_0\epsilon/2$ is the lattice energy of the perfect solid. $\Delta\rho = \Delta(N_0/V) = -(N_0/v_0)\Delta x$ and hence

$$\left(\frac{\Delta U}{\Delta\rho}\right)_{T_0,P_0} = -\frac{\epsilon}{2N_0}\frac{v_0}{\Delta x} = -\frac{\epsilon}{2}v_0 \,,$$

since $N_0\Delta x = \Delta N_v$. The first term in Eq. (1) is equal to $-N_0\epsilon/2$ and hence Eq. (1) is as follows

$$U(\rho, T_0, P_0) = -\frac{N_0\epsilon}{2} + \frac{N_0\epsilon x}{2} - \frac{N_0\epsilon\alpha'}{2}x^2 + \frac{N_0\epsilon\beta' x^3}{3} - \cdots \,, \tag{2}$$

where

$$\alpha' = -\frac{\rho_0^2}{\epsilon N_0}\left(\frac{\partial^2 U}{\partial\rho^2}\right)_{T_0,P_0}, \quad \beta' = -\frac{\rho_0^3}{2N_0\epsilon}\left(\frac{\partial^3 U}{\partial\rho^3}\right)_{T_0,P_0} .$$

Now the change in Gibbs free energy ΔF for the above process ($\Delta N_v = 1$) is as follows

$$\Delta F = \Delta U - T_0\Delta S + P_0\Delta V \,. \tag{3}$$

Hence for the material under consideration F is as follows

$$F = N_0\left(-\frac{\epsilon}{2} + \frac{\epsilon x}{2} - \frac{\alpha'}{2}\epsilon x^2 + \frac{\beta'}{3}\epsilon x^3 - \cdots\right) - TS + \frac{P v_0 N_0}{1-x} \,. \tag{4}$$

In the following we will assess the entropy S by setting it to be equal to the entropy of mixing molecules and vacancies and is equal to $S^0 = k\ln(N!/N_v!N_0!)$ where k is the Boltzmann constant and hence

$$-TS^0 = N_0 kT\left(\frac{x\ln x}{1-x} + \ln(1-x)\right) \,.$$

This approximation is an overestimate of S due to the interactions between vacancies. For most cases the excess entropy $S^0 - S$ is small compared to U/T and S^0. Hence F is a function of x (or the number N_v) and is as follows

$$\frac{F(x)}{N_0 kT} = \frac{F^{\text{vib}}(x)}{N_0 kT} + \frac{1}{kT}\left(-\frac{\epsilon}{2} + \frac{\epsilon x}{2} - \frac{\epsilon\alpha}{2}x^2 + \frac{\epsilon\beta}{3}x^3 \cdots\right) + \frac{x\ln x}{1-x} + \ln(1-x) + \frac{P v_0}{kT(1-x)} \,, \tag{5}$$

where in Eq. (5) we have separated out the vibrational free energy F^{vib} which in a later part of this paper we expand in powers of x (Sec. V). As will be shown below $w = N_0^{-1}(\partial F^{\text{vib}}/\partial x)_0 + \epsilon/2 + P_0 v_0$ for the perfect solid in the standard state at temperature T_0 and pressure P_0, where w is the work required to create a vacancy.

Let us consider the solid at temperature P_0 and T_0 and minimize the free energy with respect to x to obtain the equilibrium value of x. One obtains

$$\frac{1}{kT_0 N_0}\frac{\partial F^{\text{vib}}}{\partial x} + \frac{\ln x}{(1-x)^2} + \frac{\epsilon}{2kT_0}(1 - 2\alpha x + 2\beta x^2) + \frac{P_0 v_0}{kT_0(1-x)^2} = 0. \tag{6}$$

For small values of P_0, T_0, and x one obtains

$$-kT_0\ln x \cong \epsilon/2 + P_0 v_0 + N_0^{-1}(\partial F^{\text{vib}}/\partial x)_0 \,. \tag{7}$$

It is a general principle of statistical mechanics[6] that $x = \exp(-w/kT)$ where w is the reversible work required to change x by $\Delta x = \{(1-x)^2/N_0\}\Delta N_v = (1-x)^2/N_0$. Hence w is the work required to create a vacancy in the thermal equilibrium state of the system. Equation (7) applies to the solid at low temperatures and at larger values of T_0 (and x) the magnitudes of α, β, and $\partial F^{\text{vib}}/\partial x$ will be essential in determining the value of w.

Equation (6) predicts the existence of three distinct phases since $F(x)$ versus x gives rise to three minima and two intervening maxima in F. We shall interpret these three systems as solid (small x), liquid (intermediate values of x), and gas ($x \lesssim 1$). The three distinct phases and the corresponding values of x are graphically illustrated by plotting

$$+\frac{\ln x}{(1-x)^2} + \frac{P_0 v_0}{kT_0(1-x)^2} = f_1(x)$$

and

$$f_2(x) = -\frac{\epsilon}{2kT_0}(1 - 2\alpha x + 2\beta x^2) - \frac{\partial F^{\text{vib}}}{kT_0 N_0\partial x}$$

versus x. The points of intersection of these two functions correspond to the minima and maxima in $F(x)/N_0 kT$. This is illustrated in Fig. 1 where $f_1(x)$ and $f_2(x)$ are plotted versus x with values of α, β, $\partial F^{\text{vib}}(x)/\partial x$, and ϵ that have been determined for argon at the solid-liquid-gas triple point (Sec. III A). The dependence of $F^{\text{vib}}(x)$ on x is very nearly that determined for the hard-sphere system (Sec. V).

The gas-liquid critical constants are determined from Eq. (6) by requiring that $\partial P/\partial V = 0$ and $\partial^2 P/\partial V^2 = 0$, and one obtains the following critical constants in the limit that $\alpha = \beta = 0$ and we neglect higher derivatives of $F^{\text{vib}}(x)$ other than the first

$$x_c = \frac{1}{2}\,, \quad T_c = \frac{\epsilon}{4k} + \frac{1}{2k}\left(\frac{\partial F^{\text{vib}}}{\partial x}\right)_0 \,, \qquad P_c v_0/kT_c = \ln 2 - \tfrac{1}{2} = 0.1932 \,. \tag{8}$$

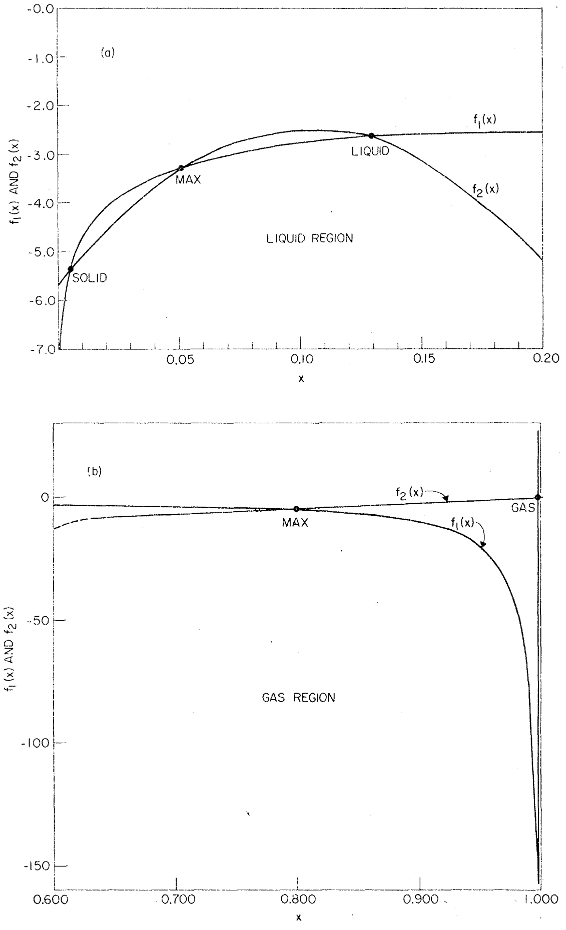

FIG. 1. (a) $f_1(x)$ and $f_2(x)$ versus x in the solid-liquid region at the triple point of argon. "Max" indicates the value of x for which maximum in the free energy occurs. (b) $f_1(x)$ and $f_2(x)$ versus x in the gas region at the triple point of argon. Dashed portion of $f_2(x)$ corresponds to the region where the effective values of α and β depend on x. For the dilute gas $\alpha = \beta = 0$.

As will be seen below, α and β decrease rapidly with increase in temperature and Eqs. (8) may be considered as a fair first approximation to the gas-liquid critical constants. If α and β are not equal to zero, one must solve a cubic equation in x to obtain the critical constants.

B. Expressions for parameters α and β

Let us reconsider the cell model of Sec. II A from a slightly different point of view. Consider N molecules occupying N cells each of volume v_0. These molecules, we will assume, interact pairwise with the potential $\phi(r)$. Now in $N_N = Nx$ of the cells, add neutralizing charges in such a way that the pair potential between a molecule in one cell and the neutralizing charges in another cell is $-\phi(r)$ and the pair potential between neutralizing charges in different cells is $\phi(r)$. In this way we create, effectively, xN empty cells and the free energy of the system may be readily evaluated.

The internal energy U of this system may be decomposed as follows

$$U = U_{mm} + U'_{mn} + U_{nn} \ , \tag{9}$$

where U_{mm} is the potential energy between the N molecules and is equal to $-\frac{1}{2}\epsilon N$. U'_{mn} is the potential energy between molecules and neutralizing charges (excluding any interactions between a molecule and neutralizing charges in the same cell) and is equal to $N_N\epsilon$. U_{nn} is the potential energy of interaction between neutralizing charges in different cells and is as follows:

$$U_{nn} = \tfrac{1}{2} N_N \rho_N \int g_N(r) \phi_N(r) \, d\vec{r} \ , \tag{10}$$

where ρ_N is equal to the number density of cells containing neutralizing charges ($\rho_N = x/v_0$), $g_N(r)$ is the vacancy radial distribution function and $\phi_N(r)$ is the pair potential between neutralizing charges in different cells $[\phi_N(r) = \phi(r)]$. We need the free energy f per molecule that has not been neutralized. This is as follows:

$$f = \frac{U}{N_0} - \frac{TS^0}{N_0} + \frac{PV}{N_0} \ , \tag{11}$$

where, as before, we have estimated the entropy by S^0, the entropy of mixing of molecules and neutralized molecules.

$$f = \frac{F(x)^{\text{vib}}}{N_0} - \frac{\epsilon}{2} + \frac{x}{1-x}\,\frac{\epsilon}{2} + \frac{x^2}{2v_0(1-x)} \int g_v(r)\phi(r)\, d\vec{r}$$
$$+ kT\,\frac{x \ln x}{1-x} + kT \ln(1-x) + \frac{Pv_0}{1-x} \ , \tag{12}$$

where we have replaced $g_N(r)$ by $g_v(r)$, the vacancy radial distribution function. By comparison of Eq. (12) with Eq. (5) one may readily obtain the following expressions for α and β:

$$-\alpha\epsilon = \epsilon + \frac{1}{v_0} \int e^{-\phi(r)/kT} \phi(r)\, d\vec{r} \ , \tag{13}$$

$$\beta\epsilon = \frac{3}{2}\epsilon + \frac{3}{2v_0^2} \int e^{-\phi(r)/kT} \phi(r) g_v^{(1)}(r)\, d\vec{r}$$
$$+ \frac{3}{2}\,\frac{1}{v_0} \int e^{-\phi/kT} \phi(r)\, d\vec{r}$$
$$= -\frac{3}{2}\alpha + \frac{3}{2} v_0^{-2} \int e^{-\phi/kT} \phi(r) g_r^{(1)}(r)\, d\vec{r} \ . \tag{14}$$

In deriving Eqs. (13) and (14) we have used the virial expansion[7] of the vacancy radial distribution function where $g_v^{(1)}(r)e^{-\phi/kT}$ is the coefficient of the vacancy density to the first power in the virial expansion.

$\alpha\epsilon$ as given by Eq. (13) may be evaluated for the LJ potential by a series expansion in ascending powers of $\epsilon_{\mathrm{LJ}}/kT$ by expansion of the exponential factor in the integrand of Eq. (13), integrating, and placing a lower limit on $r=\sigma_{\mathrm{LJ}}$. The result is as follows:

$$-\alpha\epsilon=\epsilon-4\pi\epsilon_{\mathrm{LJ}}\left[\frac{8}{9}+0.4064\left(\frac{\epsilon_{\mathrm{LJ}}}{kT}\right)+0.1478\left(\frac{\epsilon_{\mathrm{LJ}}}{kT}\right)^2+0.04041\left(\frac{\epsilon_{\mathrm{LJ}}}{kT}\right)^3+\cdots\right]. \qquad (15)$$

Hence α is determined as a function of ϵ and temperature T from Eq. (15).

The parameter β may be evaluated approximately by the following procedure. A rather accurate way of correcting the zeroth approximation to $g(r)$ is given in Ref. 8 and $g^{(1)}(r)=-v_0W(r)/kT$, where $W(r)$ is defined as the negative of the difference between the potential ϕ_{LJ} and the potential of average force. β is as follows for argon

$$\beta\epsilon=\frac{3}{2}\epsilon-4\pi\epsilon_{\mathrm{LJ}}\left[0.8143+0.3566\left(\frac{\epsilon_{\mathrm{LJ}}}{kT}\right)+0.1367\left(\frac{\epsilon_{\mathrm{LJ}}}{kT}\right)^2+0.0386\left(\frac{\epsilon_{\mathrm{LJ}}}{kT}\right)^3+\cdots\right]. \qquad (16)$$

If the vacancies are completely randomly distributed, α and β are exactly equal to zero. This may be seen by noting that U_{nn} of Eq. (10) in this case is given by

$$U_{nn}=-\tfrac{1}{2}N_N\epsilon x \qquad (17)$$

and

$$\frac{U}{N_0}=-\frac{\epsilon}{2}+\frac{\epsilon}{2(1-x)}x-\frac{\epsilon x^2}{2(1-x)}=-\frac{\epsilon}{2}+\frac{\epsilon x}{2} \qquad (18)$$

and hence, for a completely random distribution of vacancies $\alpha=\beta=0$.

Let us now examine the free energy for the dilute monatomic gas ($x\approx 1$). In this case it is clear that $\alpha=\beta=0$ and the free energy per molecule

$$f=\frac{F^{\mathrm{vib}}}{N_0}-\frac{\epsilon(1-x)}{2}+\frac{kTx\ln x}{1-x}+kT\ln(1-x)+\frac{Pv_0}{1-x}. \qquad (19)$$

We must evaluate F^{vib}/N_0 in the cell model approximation for the gas in which an occupied cell has the center of a molecule somewhere inside the cell. The translational partition function Z^{tr} for a particle in a box[9] then applies and

$$Z^{\mathrm{tr}}=(2\pi mkT)^{3/2}v_0/h^3. \qquad (20)$$

Hence $U^{\mathrm{vib}}/N_0=\frac{3}{2}kT$ and $S^{\mathrm{vib}}/N_0=\frac{3}{2}k+k\ln[v_0(2\pi mkT)^{3/2}/h^3]$. Thus

$$f=-kT\ln\left(\frac{v_0(2\pi mkT)^{3/2}}{h^3}\right)-\frac{\epsilon}{2}(1-x)+kT\left(\frac{x\ln x}{1-x}+\ln(1-x)\right)+\frac{Pv_0}{1-x}. \qquad (21)$$

But $Pv_0/(1-x)=kT$ and one obtains as $x\to 1$

$$f=-kT\ln\left(\frac{V(2\pi mkT)^{3/2}}{N_0h^3}\right)-\frac{\epsilon}{2}\frac{N_0v_0}{V}. \qquad (22)$$

For the very dilute gas the usual result is

$$f=-kT\ln\left(\frac{V(2\pi mkT)^{3/2}}{N_0h^3}\right). \qquad (23)$$

For dilute gases the term $-kT\ln[V(2\pi mkT)^{3/2}/N_0h^3]$ is much larger in magnitude than $-(\epsilon/2)N_0v_0/V$, and hence the present cell model is very nearly equal to the usual result for the dilute gas.

III. MELTING AND CONDENSATION OF ARGON

A. Melting

In order to apply the above model to a real system, one must assess the vibrational free energy $F^{\mathrm{vib}}(x)$. We will use an independent harmonic oscillator approximation in evaluating F^{vib} for solid and liquid argon. In this case U^{vib} and S^{vib} are as follows:

$$U^{\mathrm{vib}}=\frac{3RT(h\nu/kT)}{\exp(h\nu/kT)-1}, \qquad (24)$$

$$S^{\mathrm{vib}}=\frac{3R(h\nu/kT)}{\exp(h\nu/kT)-1}-3R\ln\{1-\exp(-h\nu/kT)\}. \qquad (25)$$

The effective harmonic frequency for the solid ν_s was determined from the experimental entropy[3] S_s of the solid. The vibrational contribution to S_s was calculated by subtracting from S_s the entropy ΔS_v due to the volume expansion of the solid[10]

$$\Delta S_v=(V_m-V_0)\kappa_s/\beta_s \qquad (26)$$

where V_m and V_0 are the molar volume at the melting point and at 0°K, respectively, κ_s is the volume coefficient of expansion of the solid at T_m and β_s is the isothermal compressibility at T_m. $h\nu_s/k=75$°K is obtained in this manner. The calculated constant volume specific heat C_v^s at T_m is 5.58 kcal °K^{-1} mole^{-1} in the harmonic approximation and the observed value[3] of C_v^s is 5.74 cal °K^{-1} mole^{-1}.

Next we must estimate ν_l for the liquid. This was obtained, in first approximation, from molecular-dynamics calculations on liquid argon in which the Fourier transform of the "rattling" contribution[2(b)] to the velocity autocorrelation function was used. The rattling motion of an argon atom in liquid argon may be represented to a very good degree of approximation as a damped harmonic oscillator as shown in Appendix B. In this way we obtain $h\nu_l/k = 51\,^\circ\mathrm{K}$. The calculated specific heat at constant volume $C_v^l = 5.78\ \mathrm{cal}\,^\circ\mathrm{K}^{-1}\,\mathrm{mole}^{-1}$; the observed value[11] is $5.74\ \mathrm{cal}\,^\circ\mathrm{K}^{-1}\,\mathrm{mole}^{-1}$.

Next, α and β were evaluated from Eqs. (15) and (16) at $T_m = 83.8\,^\circ\mathrm{K}$. One obtains

$$\alpha = 6189/\epsilon - 1 \tag{27}$$

and

$$\beta = \tfrac{3}{2}(-3583 + \epsilon)/\epsilon \ , \tag{28}$$

where ϵ is expressed in $\mathrm{cal\,mole}^{-1}$. At the triple point we shall set $\epsilon = \epsilon_l = \epsilon_s$ in the following.

$F^{\mathrm{vib}}(x)/kT$ is expanded in a power series in x in Sec. V [Eq. (47)], and we shall use the ratio of free volume v_1^f/v_0^f determined for hard spheres to evaluate $\Delta F^{\mathrm{vib}}(x)$ except for v_2^f/v_1^f and v_3^f/v_2^f which we will adjust (as done in Sec. V) and these are the only adjustable parameters in the present calculations.

We have determined the melting parameters by requiring that $f_s = f_l$ and in addition that $\partial f_l/\partial x = \partial f_s/\partial x = 0$. Calculated melting data are given in Table I and compared with the observed values. The values of the adjusted parameters are $v_2^f/v_1^f = 2.312$ and $v_3^f/v_2^f = 2.104$ which are very close to those determined for hard spheres [Sec. V, Eqs. (48)]. In Table II we give an account of the various contributions to the change in internal energy $(U_l - U_s)/RT$ and change in entropy $(S_l - S_s)/R$ upon melting. The value of $h\nu_l/k$ corresponding to $\Delta F^{\mathrm{vib}}/RT$ is $46\,^\circ\mathrm{K}$ in close proximity to the value obtained above ($51\,^\circ\mathrm{K}$) from the molecular-dynamics calculations on argon. We have assigned the difference

$$\Delta U^{\mathrm{vib}} + \Delta U_\epsilon - T\Delta S^{\mathrm{vib}} - T\Delta S^{\mathrm{config}} + P\Delta V_m$$

to communal entropy which turns out to be somewhat smaller than the corresponding value[7] for hard spheres ($\Delta S^{\mathrm{comm}}/k = 0.168$). $\Delta S^{\mathrm{config}}$ is defined in Table II. The change in vibrational entropy is 73% of the total change in entropy upon melting in the present model.

TABLE I. Melting data for argon.

Quantity	Model	Experiment
T_m (°K)	81.7	83.8 [a]
ΔU ($\mathrm{cal\,mole}^{-1}$)	311	281 [a]
ΔV_m ($\mathrm{cm}^3\,\mathrm{mole}^{-1}$)	3.69	3.79 [a]
ΔH_{vap} ($\mathrm{cal\,mole}^{-1}$)	1521	1550 [a]
$C_p^s - C_v^s$ ($\mathrm{cal\,mole}^{-1}\,^\circ\mathrm{K}^{-1}$)	2.704	2.589 [b]
$C_p^l - C_v^l$ ($\mathrm{cal\,mole}^{-1}\,^\circ\mathrm{K}^{-1}$)	5.87	5.10 [a]
P_m (atm)	0.443	0.679 [a]
x_s	3.70×10^{-3}	3.74×10^{-3} [c]
x_l	0.130	0.133 [d]
$(\partial x/\partial T)_p$ ($^\circ\mathrm{K}^{-1}$)	2.537×10^{-3}	2.54×10^{-3} [d]
β_l ($10^6\,\mathrm{atm}^{-1}$)	305	200 [a]
$(dP/dT)_m$ ($\mathrm{atm}\,^\circ\mathrm{K}^{-1}$)	33.9	39 [a]

[a] *Argon, Helium and The Rare Gases*, edited by G. A. Cook (Interscience, New York, 1961).

[b] See Ref. 3.

[c] G. F. Nardelli and A. R. Chiarotti, Nuovo Cim. 18, 1053 (1960).

[d] x_l, $(\partial x/\partial T)_l$ were calculated from the equation $\rho_l = \rho_s(1 - x_l)$.

TABLE II. Contributions to $\Delta U_m/kT$ and $\Delta S_m/k$ at the triple point for argon.

$\Delta U^{\mathrm{vib}}/kT$	0.396	$\Delta S^{\mathrm{vib}}/k$	1.406
$\Delta U_\epsilon/kT$ [a]	1.521	$\Delta S^{\mathrm{config}}/k$	0.424 [b]
		$\Delta S^{\mathrm{comm}}/k$	0.087
Total $\Delta U_m/kT$	1.917	Total $\Delta S_m/k$	1.917

[a] $\Delta U_\epsilon/kT = (\epsilon/2kT)(x_l - x_s - \alpha x_l^2 + \tfrac{2}{3}\beta x_l^3)$.

[b] $\Delta S^{\mathrm{config}}/k = x_s \ln x_s/(1 - x_s) + \ln(1 - x_s) - x_l \ln x_l/(1 - x_l) - \ln(1 - x_l)$.

In the following we will explain how the melting data in Table I were computed from the model. ϵ was computed from the experimental heat of sublimation ΔH_{subl} as follows

$$\tfrac{1}{2}\epsilon = \Delta H_{\mathrm{subl}} + U_s^{\mathrm{vib}} - \tfrac{3}{2}RT \tag{29}$$

at T_m, $\epsilon/2 = 1900\ \mathrm{cal\,mole}^{-1}$. The heat of vaporization ΔH_{vap} was computed from the parameters as follows:

$$\Delta H_{\mathrm{vap}} = \tfrac{1}{2}\epsilon - \tfrac{1}{2}\epsilon(x_l - \alpha x_l^2 + \tfrac{2}{3}\beta x_l^3) - U_l^{\mathrm{vib}} + \tfrac{3}{2}RT \ . \tag{30}$$

Equation (30) follows by setting $\Delta H_{\mathrm{vap}} = U_l - U_{\mathrm{vap}}$. Next $C_p^s - C_v^s$ was computed from the thermodynamic relation

$$C_p - C_v = \left[P\left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \ . \tag{31}$$

The pressure is negligible at the triple point in Eq. (31) and $(\partial U/\partial V)_T$ was computed from lattice sums[12] for $\epsilon_s/2$ and $(\partial V/\partial T)_P$ was taken from Ref. 3. $C_p^l - C_v^l$ was computed by differentiating U^l with respect to T at constant pressure and at constant volume and subtracting the results

$$C_p^l - C_v^l = -\frac{1}{2}\left(\frac{\partial\epsilon}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \frac{\epsilon}{2}(1 - 2\alpha x_l + 2\beta x_l^2)\left(\frac{\partial x}{\partial T}\right)_P + \frac{1}{2}\left(\frac{\partial\epsilon}{\partial T}\right)_P (x_l - \alpha x_l^2 + \tfrac{2}{3}\beta x_l^3) \ , \tag{32}$$

where we have set $(\partial\epsilon/\partial T)_V = 0$. The first term on the right-hand side of Eq. (32) was placed equal to $(\partial U^s/\partial V)_T(\partial V/\partial T)_P$ for the solid.

The pressure at the triple point, P_m, was computed by equating the free energy of the solid to the free energy of the gas [Eq. (22)]. Neglecting terms in x_s this is as follows:

$$-T\Delta S_v + F_s^{\mathrm{vib}} - \frac{\epsilon}{2} = -RT\ln\left(\frac{V(2\pi mkT)^{3/2}}{Nh^3}\right) \quad , \qquad (33)$$

but to an excellent degree of approximation $V = RT/P$ with the result that the pressure P_m may be obtained from Eq. (33).

The value of x_s was calculated from the following equation which is obtained by setting $\partial f/\partial x = 0$:

$$\frac{N_0^{-1}}{kT}\left(\frac{\partial F^{\mathrm{vib}}}{\partial x}\right)_s + \frac{\ln x_s}{(1-x_s)^2} = -\frac{\epsilon}{2kT}(1-2\alpha x_s + 2\beta x_s^2) \ . \qquad (34)$$

$(\partial x_l/\partial T)_P$ was obtained from Eq. (6) by differentiation with respect to T at constant pressure:

$$\left(\frac{\partial x_l}{\partial T}\right)_P = \frac{A}{B} \qquad (35)$$

where

$$A = \frac{(\partial F^{v\epsilon}/\partial x)_l}{kT^2} - \frac{1}{2kT}\left(\frac{\partial\epsilon}{\partial T}\right)_P(1-2\alpha x_l + 2\beta x_l^2)$$

and

$$B = \frac{1}{x_l(1-x_l)^2} + \frac{2\ln x_l}{(1-x_l)^3} + \frac{1}{kT}\left(\frac{\partial^2 F^{v\epsilon}}{\partial x^2}\right)_l \ ,$$

where $F^{v\epsilon}$ is the sum of the vibrational free energy and U_ϵ (Table II).

The isothermal compressibility for the liquid was obtained by differentiating the equation $\rho_l = \rho_s(1-x_l)$ with respect to P at constant temperature. One obtains

$$\beta_l = \beta_s - \frac{1}{(1-x_l)}\left(\frac{\partial x_l}{\partial P}\right)_T \qquad (36)$$

and $(P=0)$

$$\left(\frac{\partial x_l}{\partial P}\right)_T = \frac{A'}{B'} \qquad (37)$$

where

$$A' = -\frac{v_0}{kT(1-x_l)^2} - \frac{1}{2kT}\left(\frac{\partial\epsilon}{\partial P}\right)_T(1-2\alpha x_l + 2\beta x_l^2)$$

and

$$B' = \frac{1}{x_l(1-x_l)^2} + \frac{2\ln x_l}{(1-x_l)^3} + \frac{1}{kT}\left(\frac{\partial^2 F^{v\epsilon}}{\partial x^2}\right)_l$$

with the result that $(P=0)$

$$\beta_l = \beta_s + \frac{C}{D} \qquad (38)$$

where

$$C = \frac{v_0}{kT}\frac{x_l}{(1-x_l)} + \frac{1}{2kT}\left(\frac{\partial\epsilon}{\partial P}\right)_T(1-2\alpha x_l + 2\beta x_l^2)\,x_l(1-x_l)$$

and

$$D = 1 + \frac{2x_l\ln x_l}{(1-x_l)} + \frac{1}{kT}\left(\frac{\partial^2 F^{v\epsilon}}{\partial x^2}\right)_l x_l(1-x_l)^2 \ .$$

Finally, the slope of the melting curve at zero pressure, $(dP/dT)_m$ was obtained by equating f_l and f_s and differentiating with respect to T. The result is as follows

$$\left(\frac{dP}{dT}\right)_m = \frac{A''}{B''} \qquad (39)$$

where

$$A'' = \frac{-\Delta F_{ls}^{v\epsilon}}{kT^2} + \frac{1}{kT}\left(\frac{\partial F^v}{\partial x}\right)_l\left(\frac{\partial x_l}{\partial T}\right)_P - \frac{1}{kT}\left(\frac{\partial F^{v\epsilon}}{\partial x}\right)_s\left(\frac{\partial x_s}{\partial T}\right)_P$$
$$+ \frac{1}{2kT}\left(\frac{\partial\epsilon}{\partial T}\right)_P(x_l - x_s - \alpha x_l^2 + \tfrac{2}{3}\beta x_l^3)$$
$$+ \frac{\ln x_l}{(1-x_l)^2}\left(\frac{\partial x_l}{\partial T}\right)_P - \frac{\ln x_s}{(1-x_s)^2}\left(\frac{\partial x_s}{\partial T}\right)_P$$

and

$$B'' = -\frac{1}{kT}\left(\frac{\partial F^{v\epsilon}}{\partial x}\right)_l\left(\frac{\partial x^l}{\partial P}\right)_T$$
$$+ \frac{1}{kT}\left(\frac{\partial F^{v\epsilon}}{\partial x}\right)_s\left(\frac{\partial x_s}{\partial P}\right)_T - \frac{v_0}{kT(1-x_l)}$$
$$+ \frac{v_0}{kT(1-x_s)} - \frac{\ln x_l}{(1-x_l)^2}\left(\frac{\partial x_l}{\partial P}\right)_T + \frac{\ln x_s}{(1-x_s)^2}\left(\frac{\partial x_s}{\partial P}\right)_T$$
$$- \frac{1}{2kT}\left(\frac{\partial\epsilon}{\partial P}\right)_T(x_l - x_s - \alpha x_l^2 + \tfrac{2}{3}\beta x_l^3) \ .$$

The melting curve of argon was computed from the model and is shown in Fig. 2. The agreement is good in view of the fact that no additional adjustable parameters were used in the calculation. The vapor pressure of the solid and liquid versus temperature was computed and is given in Fig. 3 where $\log_{10}P$ is plotted versus $1/T$ and compared with experiment.

B. Condensation

In the following we shall calculate the critical temperature, pressure, and density from Eq. (9) using the value of ϵ determined by extrapolating lattice parameter data[3] versus temperature to 150 °K to obtain v_0 and then calculation of ϵ at 150 °K (reference solid) using lattice sums.[12] $(\partial F/\partial x)_0$ will be placed equal to the value used at the triple point and found for hard spheres (Sec. V). In this way we obtain $v_0 = 31.9$ cm^3 mole^{-1} (at the triple point $v_0 = 25.7$ cm^3 mole^{-1}) and $\epsilon = 3205$ kcal mole^{-1}. Values of T_c, P_c, and ρ_c calculated

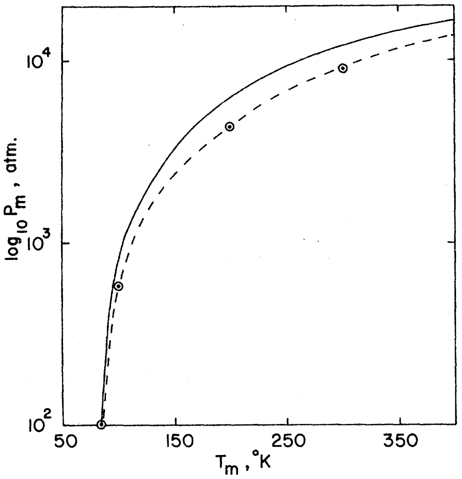

FIG. 2. Melting pressure P_m versus temperature for solid argon as given by the present model (---0---) and from experiment (———).

in this fashion are given in Table III along with the experimental values. The expression for T_c in Eq. (8) demonstrates why a system of hard spheres has no liquid phase or critical point since in this case $\epsilon = 0$ and $(\partial F^{\text{vib}}/\partial x)_0$ is negative [Eq. (47), Sec. V].

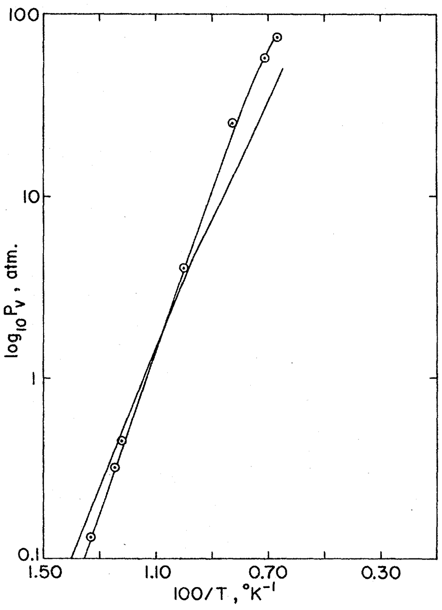

FIG. 3. Vapor pressure of solid and liquid argon versus $100/T$ for the model (——0——) and experiment (———).

TABLE III. Observed and calculated gas-liquid critical constants.

	Model ($\alpha = \beta = 0$)	Expt.
T_c (°K)	148.7	150.9
P_c (atm)	74.0	48.3
ρ_c (g cm^{-3})	0.626	0.536

The extrapolation of lattice parameter[3] data versus temperature was done by using the cell model for the solid. The experimental data are very accurate and the temperature dependence of the lattice parameter was closely given by the cell model up to the melting point. The coexistence curve between liquid and vapor is shown in Fig. 4 and compared with the results of the present model. The agreement is good over the entire range of densities.

IV. PAIR CORRELATION FUNCTION

In this section we will compute the pair correlation function $g(r)$ for liquid argon in the quasilattice model approximation and compare the results with the $g(r)$ computed by machine.[2(a)] For a Gaussian distribution of atomic coordinates in three dimensions, a component of $g(r)$, $g_\alpha(r)$ due to the atoms located at distance r_0 from the origin, will be given by (Appendix C)

$$g_\alpha(r) = \frac{\gamma_\alpha \alpha^{1/2} N_\alpha e^{-\alpha(r-r_0)^2}(1-x)}{4\pi\sqrt{\pi}\,\rho_l r r_0}, \qquad (40)$$

where $\alpha^{1/2} = 2^{-1/2}\langle (r-r_0)^2\rangle^{-1/2}$, N_α is the number of atoms located at r_0, ρ_l is the liquid number density, γ_α is a normalizing factor near unity and

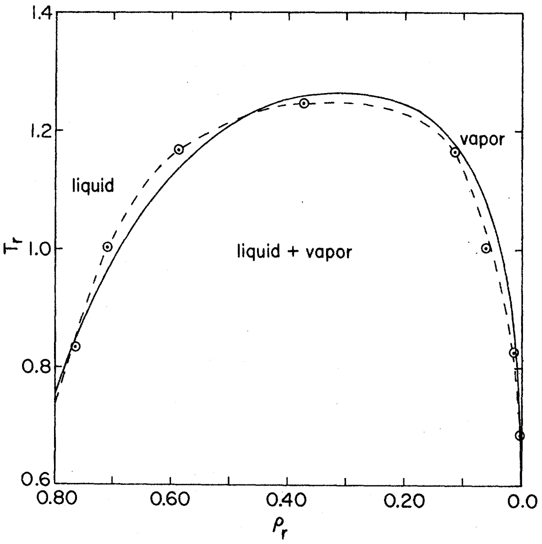

FIG. 4. Coexistence curve of liquid and vapor as computed from the cell model (---0--) and experiment (———).

TABLE IV. Quantities used in the calculation of the radial distribution function for argon.

Coordinates	r_0	r_0 (Å)	r_0/σ	N_α	$\langle (r-r_0)^2\rangle_\alpha^{1/2}$ (Å)	$g_\alpha(r_0)$
$\frac{1}{2}\frac{1}{2}0$	a	3.816	1.123	12	0.392	2.782
100	$\sqrt{2}a$	5.396	1.587	6	1.0	0.267
$1\frac{1}{2}\frac{1}{2}$	$\sqrt{3}a$	6.610	1.944	24	0.92	0.776
110	$2a$	7.633	2.245	12	0.85	0.314
$\frac{3}{2}\frac{1}{2}0$	$\sqrt{5}a$	8.534	2.510	24	1.2	0.356
111	$\sqrt{6}a$	9.350	2.750	8	1.0	0.119
$\frac{3}{2}1\frac{1}{2}$	$\sqrt{7}a$	10.098	2.970	48	1.0	0.611
200	$2\sqrt{2}a$	10.792	3.174	8	1.2	0.074
$\frac{3}{2}\frac{3}{2}0$	$3a$	11.451	3.368	12	1.2	0.100
$2\frac{1}{2}\frac{1}{2}$	$3a$	11.451	3.368	24	1.2	0.199
210	$\sqrt{10}a$	12.067	3.549	24	1.2	0.178
$\frac{3}{2}\frac{3}{2}1$	$\sqrt{11}a$	12.658	3.723	24	1.2	0.162
211	$2\sqrt{3}a$	13.220	3.888	24	1.2	0.148
$\frac{5}{2}\frac{1}{2}0$	$\sqrt{13}a$	13.759	4.047	24	1.2	0.138
$2\frac{3}{2}\frac{1}{2}$	$\sqrt{13}a$	13.759	4.047	48	1.2	0.275
				Total 322		

x as before is the probability of a vacancy at a lattice site. The vacancies are assumed to be distributed in a random fashion [$\gamma_\alpha \sim 0.99$, obtained by numerical integration of Eq. (40)]. The coordinates, distances (r_0), N_α, $\langle (r-r_0)^2\rangle^{1/2}$, and $g_\alpha(r_0)$ are given in Table IV for a face-centered-cubic lattice with $a = 2^{1/6}\sigma_{\text{LJ}} = 3.816$ Å out to the first 322 nearest neighbors.

The quantities $\langle (r-r_0)^2\rangle^{1/2}$ were adjusted to give the best fit to $g(r)$, but the selected values are readily shown, in the quasilattice cell model approximation, to the quite reasonable. In a classical machine calculation, the most probable value of v_z^2, the square of a component of velocity, is given by kT/m. For the nearest neighbors, the value of $\langle (r-r_0)^2\rangle^{1/2}$ is determined essentially by the second derivative of the potential of average force $\phi^*(r)$ at the maximum in $g(r)$. This is strictly true in a classical harmonic approximation where the distribution of $g_\alpha(r)$ is Gaussian. This may be seen as follows. At the turning points of the harmonic oscillator

$$\tfrac{1}{2}mv_z^2 = kT = \tfrac{1}{2}Kz_m^2 \tag{41}$$

where K is the force constant and z_m is the maximum value of z at the energy $kT/2$. But for the potential of average force for nearest neighbors

$$K = -\frac{kT}{g(r)}\left(\frac{d^2g}{dr^2}\right)_{r=r_0} \tag{42}$$

$$\cong 2\alpha kT \ , \tag{43}$$

where the last result follows for nearest neighbors where $g(r)$ is determined primarily by the Gaussian centered at $r = r_0$ for nearest neighbors. Hence from Eqs. (41) and (43), $z_m = (\alpha)^{-1/2} = 2^{1/2}\langle (r-r_0)^2\rangle^{1/2}$ which is exactly true for a harmonic potential and hence $\langle (r-r_0)^2\rangle^{1/2}$ is determined by the curvature of $g(r)$ at $r = r_0$. The shape of $g(r)$ for the first nearest neighbors will be essentially the same as $\phi^*(r)$, i.e., a lopsided distribution which tails off relatively slowly with increase in $r - r_0$.

For other than first nearest neighbor molecules, $\langle (r-r_0)^2\rangle^{1/2}$ is determined classically by the potential of average force in the vicinity of a lattice site with perfectly reflecting walls at the cell boundary and hence for distant neighbors for which $\phi^*(r)/kT \approx 0$ the values of $\langle (r-r_0)^2\rangle^{1/2}$ are comparable to the cell dimensions.

In Fig. 5 is given the results of the machine calculation[2(a)] at 94 °K for argon and the computed $g(r)$ for the present quasilattice approximation. The agreement is excellent and this lends support to the validity of the present quasilattice approximation for liquid argon.

V. MELTING OF A SYSTEM OF HARD SPHERES

The present cell model may be used to study melting of a hard-sphere system. Hard spheres

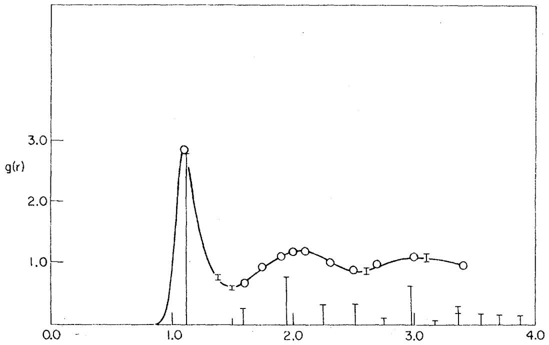

FIG. 5. Pair correlation function $g(r)$ of argon at 94°K as computed in Ref. 2(a) (———). Circled points are calculated from the cell model as described in Sec. IV. Vertical bars are the values of $g_\alpha(r_0)$. Statistical error in machine computations is indicated.

exhibit a first-order melting transition[7] with $v_s = 1.359v_0^0$, $v_l = 1.499v_0^0$, and $Pv_0^0/kT = 8.27$ where v_0^0 is the atomic volume for the cubic close-packed structure at 0°K. Due to the lack of interaction of hard spheres except at contact, the communal entropy[7] S^{comm} is important in determining the transition. In the present model the free energy of a system of hard spheres is as follows

$$\frac{F^{\text{HS}}}{kT} = \frac{F^{\text{vib}}(x)}{kT} - \frac{S^{\text{comm}}(x)}{k} + \frac{x \ln x}{1-x} + \ln(1-x) + \frac{Pv_0}{kT(1-x)} \quad . \tag{44}$$

The vibrational free energy will be determined by the free volume v^f available to a hard sphere and classically is as follows:

$$\frac{F^{\text{vib}}}{kT} = -\ln\left(\frac{v^f(2\pi mkT)^{3/2}}{h^3}\right) \quad . \tag{45}$$

The free volume will be a function of x and will be larger in the fluid phase than in the solid.

The empty cells in a hard-sphere fluid will be distributed, in first approximation, at random and hence let us compute the vibrational free energy in the fluid as follows using the binomial expansion of $(1-x+x)^{12}$ and weighting the vibrational free energy of a sphere in the presence of n vacancies by the nth binomial coefficient. This procedure is valid in an independent-particle approximation:

$$-\frac{F^{\text{vib}}(x)-F^{\text{vib}}(0)}{kT} = 12(1-x)^{11}x\ln\left(\frac{v_1^f}{v_0^f}\right) + 66(1-x)^{10}x^2\ln\left(\frac{v_2^f}{v_0^f}\right) + 220(1-x)^9x^3\ln\left(\frac{v_3^f}{v_0^f}\right) + \cdots \quad , \tag{46}$$

where v_n^f is the free volume of a hard sphere in the presence of n nearest-neighbor cells that are vacant. We may easily compute the first three derivatives of Eq. (46), evaluate at $x=0$ and obtain $\Delta F^{\text{vib}}(x)/kT$ as follows $[\Delta F^{\text{vib}}(x) = F^{\text{vib}}(x) - F^{\text{vib}}(0)]$:

$$\frac{\Delta F^{\text{vib}}(x)}{kT} = -12x\ln\left(\frac{v_1^f}{v_0^f}\right) - 66x^2\ln\left(\frac{v_2^f v_0^f}{(v_1^f)^2}\right) + 220x^3\ln\left(\frac{(v_2^f)^3 v_0^f}{(v_1 f)^3 v_3^f}\right) + \cdots \tag{47}$$

and hence we have the vibrational free energy as a function of x in terms of the quantities v_n^f. Equation (44) now yields a first-order melting transition with the melting data given in Table V along with the available experimental (machine) data. The quantities v_n^f are as follows:

$$\frac{v_1^f}{v_0^f} = 1.649, \quad \frac{v_2^f}{v_1^f} = 2.066, \quad \frac{v_3^f}{v_2^f} = 2.407 \quad . \tag{48}$$

The parameters v_n^f/v_{n-1}^f $(n=1-3)$ and the melting data of Tables V and VI were determined by requiring that $F_s^{\text{HS}} = F_l^{\text{HS}}$ and $\partial F_s^{\text{HS}}/\partial x = \partial F_l^{\text{HS}}/\partial x = 0$ and adjusting the three parameters to obtain the best fit to the machine data. S^{comm} was taken from the data given in Ref. 7 but is only a small part (13%) of the total change in PV on melting (Table VI). This procedure is only approximate for two reasons: (1) in the present model the cell size is constant and for the perfect solid and ideal gas $S^{\text{comm}} = 0$. In Ref. 7 the cell size is determined by the volume per molecule but this cell volume is only 10% bigger than in our model and hence S^{comm} of Ref. 7 is a good approximation to our S^{comm}; (2) it is expected that a small part of the S^{comm} of Ref. 7 is contained in our F^{vib}, but this contribution is essentially equal to zero for the solid at the melting point and because of our definition of ΔF^{vib} [Eq. (46)] is also very small for the fluid. An approximate derivation of S^{comm} is given in Appendix D. In Table VI we list the various contributions to $P\Delta V_m/kT$. The vibrational free energy constitutes the major part (58%) of the total change in PV.

The change in volume between T_m and 0°K is

TABLE V. Melting data for hard spheres.

Quantity	Model	Experiment[a]
Pv_0/kT	11.24	11.24±0.18
$v_0\rho_s$	1.000	1.000±0.004
$v_0\rho_l$	0.900	0.906±0.004
x_s	5.1×10^{-3}	$\sim10^{-5}$
x_l	0.100	0.0938±0.008

[a] See Ref. 7.

TABLE VI. Contributions to $P\Delta V_m/kT$.

		Theory	Expt.
Configurational[a]	$\Delta S^{\text{config}}/k$	0.361	
Communal	$\Delta S^{\text{comm}}/k$	0.168	
Vibrational	$\Delta F^{\text{vib}}/kT$	0.733	
	Total ($P\Delta V_m/kT$)	1.262	1.16±0.12

[a] $\Delta S^{\text{config}}/k = x_l \ln x_l/(1-x_l) + \ln(1-x_l)$.

known and hence Pv_0/nkT is determined since $P(v_0 - v_0^0) = 3kT$ since, from the simple cell model for the equation of state of the solid $C_p - C_v = 3R$. The change in nonvibrational internal energy on heating the perfect hard-sphere solid at P at 0°K to T_m at P is zero and hence $P\Delta V = 3kT$. In this way we obtain $Pv_0^0/NkT = 8.356$.

In Fig. 6 we present a plot of $\log(v_s - v_f)/v_s$ versus $1/T$ for the fluid, which according to the cell model for the fluid, should yield a straight line with slope equal to w/k where w is the reversible work required to form a vacancy in the fluid. A straight line results down to $Pv_0^0/NkT = 1.000$ and the slope yields $w/kT_m = 1.952$. A simple calculation[13] of the isothermal compressibility β_f of a fluid containing vacancies yields the following relationship between β_f and x_f,

$$\beta_f \cong \frac{x_f V_m}{3.25(1-x_f)RT} \tag{49}$$

and Eq. (49) predicts that a plot of $\log(N\beta_f kT/v_0^0)(1-x_f)$ versus $1/T$ should yield a straight line of slope w/k. A plot for the hard-sphere fluid is shown in Fig. 7 and the slope yields $w/kT_m = 2.075$ in good agreement with the value of w/kT_m determined from the density plot. Equation (35), when applied to hard spheres, yields a good representation of β_f also. The above facts strongly indicate that hard-sphere vacancies occur in the hard-sphere fluid at high densities.

Finally in Fig. 8 we show the equation of state for the hard-sphere system as determined by machine and compared with the results of the present model. The agreement is good over the entire range of density and pressure, particularly in the fcc solid phase.

VI. DISCUSSION

Most theories of melting that are of current interest are based on the order-disorder lattice model of Lennard-Jones and Devonshire[14] or on the hard-sphere transition modified to take into account the attractive forces.[15] In the present cell model, the presence of vacancies and the change in vibrational free energy between solid and liquid are of paramount importance. The agreement between the calculated and observed melting data (Table I) and the agreement between the observed and calculated $g(r)$ (Fig. 5) indicate that this approach is correct. The present theory describes all three states of matter: liquid, solid and gas and will yield accurate results on melting and condensation. Attractive forces play a vital role in the present theory since they determine the vacancy interaction parameters α and β and energy ϵ. The present model represents the first-order

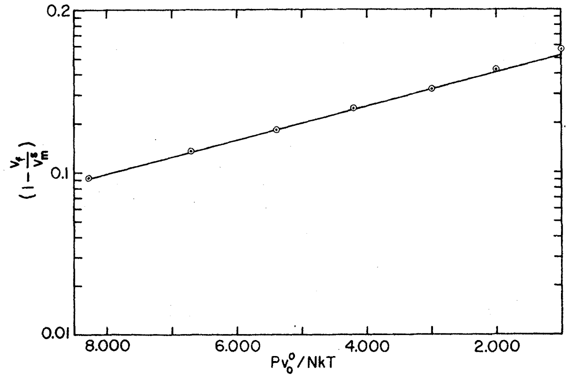

FIG. 6. $\log(1 - v_m^s/v_f)$ versus Pv_o^0/NkT for the hard-sphere fluid.

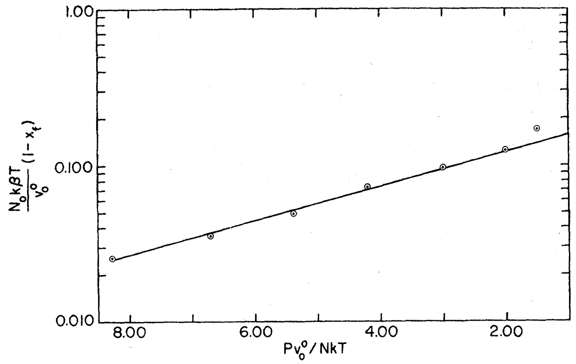

FIG. 7. $\log N\beta_f kT(1 - x_f)/v_o^0$ versus Pv_o^0/NkT for the hard-sphere fluid.

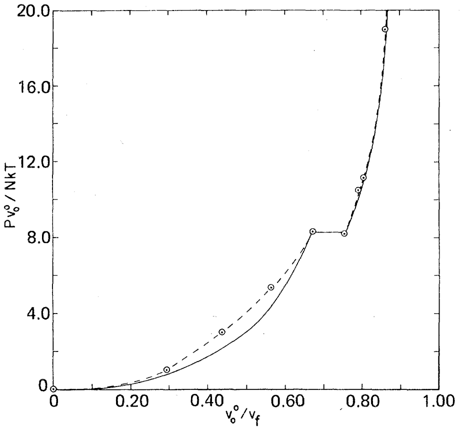

FIG. 8. Equation of state for the hard-sphere system from the vacancy-cell model (---0---) and machine experiments (———).

melting transition as an "avalanche of vacancies" since x increases by a factor of about 50 for hard spheres and a factor of 35 for argon upon melting.

The empirical melting criterion of Hansen and Verlet[16] which states that the first peak in the Fourier transform of $g(r)$ in the fluid has a constant height along the freezing curve is reasonable in the present model since $(dx/dT)_m$ is of the order of $-1\times 10^{-3}\,{}^\circ\mathrm{K}^{-1}$ along the freezing curve, and hence $g(r)$ will not change rapidly with freezing temperatures. The Lindemann melting law which states that a solid melts when the average amplitude of vibration of the atoms reaches about 10% of the nearest-neighbor distance is a consequence of the theory for hard spheres (Sec. V).

APPENDIX A: EVALUATION OF ΔU UPON VACANCY FORMATION IN THE PERFECT SOLID

In the perfect solid [$\phi(\vec{r}_i-\vec{r}_j)$ is the pair potential between molecules i and j]

$$U_{\text{initial}}=U_{\text{initial}}^{\text{vib}}+\frac{1}{2}\sum\sum_{i\neq j}\phi(\vec{r}_i-\vec{r}_j)\ . \tag{A1}$$

Now we consider the solid with one vacancy in the interior and the removed molecule k on the surface

$$U_{\text{final}}=U_{\text{final}}^{\text{vib}}+\frac{1}{2}\sum\sum_{i\neq j}\phi(\vec{r}_i-\vec{r}_j)$$
$$-\sum_{i\neq k}\phi(\vec{r}_i-\vec{r}_k)+\sum_{i\neq k}\phi(\vec{r}_i-\vec{r}_k^{\,\prime})$$

where $\vec{r}_k$ is the initial radius vector of molecule k and $\vec{r}_k^{\,\prime}$ is the final radius vector of molecule k on the surface. Let $-N_0\epsilon/2=\frac{1}{2}\sum\sum_{i\neq j}\phi(\vec{r}_i-\vec{r}_j)$ then on the average $\sum_{i\neq k}\phi(\vec{r}_i-\vec{r}_k^{\,\prime})=-\epsilon/2$ and hence (neglecting relaxational effects)

$$U_{\text{final}}=U_{\text{final}}^{\text{vib}}+\epsilon-\epsilon/2-N_0\epsilon/2\ ,$$
$$\Delta U=\Delta U^{\text{vib}}+\epsilon/2\ .$$

APPENDIX B: RATTLING MOTION OF ATOMS IN LIQUID ARGON

We will represent the rattling motion[2(a)] of atoms in computer liquid argon by the following normalized velocity autocorrelation function:

$$\psi_R(t)=f_R\cos\omega_0 t\,e^{-t/\tau_c}\ , \tag{B1}$$

where f_R is the fraction of the time spent in the rattling state, ω_0 is the harmonic angular frequency and τ_c is the mean time between hard collisions. The Fourier transform of $\psi_R(t)$ is as follows:

$$F_R(\omega)=\frac{2}{\pi}\int_0^\infty\cos\omega t\,\psi_R(t)\,dt\ ;$$

hence

$$F_R(\omega)=\frac{f_R}{\pi}\left(\frac{\tau_c}{1+(\omega+\omega_0)^2\tau_c^2}+\frac{\tau_c}{1+(\omega-\omega_0)^2\tau_c^2}\right)\ . \tag{B2}$$

From the graphs of Ref. 2(a) we obtain $f_R=0.60$, $\omega_0=7.0\times 10^{12}\ \mathrm{sec}^{-1}$ and $\tau_c=3.1\times 10^{-13}$ sec (at 94 °K). Equation (B2) provides an excellent representation of the experimental $F_R(\omega)$ given in Ref. 2(a).

APPENDIX C: GAUSSIAN COMPONENTS OF THE PAIR CORRELATION FUNCTION

We wish to compute $g_\alpha(r)$ for a three-dimensional Gaussian distribution of atomic coordinates relative to a lattice site at $r=r_0$. The normalized three-dimensional Gaussian distribution is as follows:

$$G(\vec{r})=\frac{\alpha^{3/2}}{\pi\sqrt{\pi}}\,e^{-\alpha(\vec{r}-\vec{r}_0)^2}\ . \tag{C1}$$

We must calculate $G(r)$ by integrating $G(\vec{r})$ over a spherical shell of radius $\vec{r}$. Let $\vec{r}^{\,\prime}=\vec{r}-\vec{r}_0$ then

$$r'^2=r^2+r_0^2-2rr_0\cos\theta\ , \tag{C2}$$

and we integrate over ϕ and θ. The result is as follows:

$$G(r)=(\alpha^{1/2}/\sqrt{\pi}\,rr_0)e^{-\alpha(r-r_0)^2} \tag{C3}$$

to an excellent degree of approximation for cases of interest here. Let N_α be the number of atoms located at $\vec{r}_0$. Then by definition

$$4\pi\rho_l r^2 g_\alpha(r)\,dr=N_\alpha(1-x)G(r)r^2\,dr \tag{C4}$$

and one obtains Eq. (47).

APPENDIX D: CALCULATION OF COMMUNAL ENTROPY

In this appendix we give an approximate derivation of S^{comm} for our cell model. We consider double occupancy of a cell as well as empty and singly occupied cells as done in Sec. II A. Let N be the number of cells and N_0 the number of molecules as before. Let N_v by the number of vacant cells, N_s the number of singly occupied cells, and N_d the number of doubly occupied cells. As before $N = N_0/(1-x)$ and $N_v = [(x+P_d)/(1-x)]N_0$ and the communal entropy is defined as the difference in entropy between that of the present model and that computed as in Sec. II A. That is

$$S^{\text{comm}} = k \ln\left(\frac{N!\,2^{N_d}}{N_v!N_s!N_d!}\right) - k \ln\left(\frac{N!}{N_v!N_0!}\right) . \qquad \text{(D1)}$$

Let P_d be the probability that a cell is doubly occupied; hence we obtain

$$N_d = \frac{P_d N_0}{1-x}, \quad N_s = N_0 - 2N_d = \left(\frac{1-x-2P_d}{1-x}\right) N_0 , \qquad \text{(D2)}$$

and hence

$$\frac{S^{\text{comm}}}{k} = -\frac{x}{1+x}\ln(x+P_d) - \frac{P_d}{1-x}\ln\left(\frac{x+P_d}{1-x}\right) + \frac{x\ln x}{1-x} - P_d \ln P_d - \frac{1-x-2P_d}{1-x}\ln\left(\frac{1-x-2P_d}{1-x}\right) + P_d \ln 2 . \qquad \text{(D3)}$$

To calculate P_d easily, we assume spherical cells of radius equal to half the nearest-neighbor distance in the solid (r_0). Let $\vec{a}$ be the radial vector from the center of the cell to the first molecule and then by the definition of P_d and $g(R)$ it follows that

$$P_d = \rho^2 \int_{v_0} d\vec{a} \int_{v_2(a)} g(\vec{r})\, d\vec{r} , \qquad \text{(D4)}$$

where ρ is the number density of the material and $v_2(a)$ is the volume available to molecule 2 with molecule 1 located at radius vector $\vec{a}$ such that molecule 2 is somewhere inside the volume v_0 of the cell. Transform the integral over $\vec{r}$ to an integral over $\vec{R}$ where $\vec{R}$ is the radius vector between the two molecules both of which are somewhere inside the cell. Then the integral over $\vec{R}$ reads as follows:

$$2\pi \int_{2\sigma_0}^{r_0+a} \int_{-1} r_0^2 + a^2 - \frac{4\sigma_0^2}{2ar_0} \frac{g(R)R\,dR\,d\cos\theta}{(R^2 - a^2\sin^2\theta)^{1/2}} \times \{a^2\cos 2\theta + R^2 + 2a\cos\theta\,(R^2 - a^2\sin^2\theta)^{1/2}\} , \qquad \text{(D5)}$$

where the vector $\vec{a}$ is taken as the polar axis and $2\sigma_0$ is the value of R for which $g(R) = 0$. However, $R^2 \gg a^2\sin^2\theta$ $(\cos\theta \approx -1)$ and hence the integral over $\vec{R}$ now becomes

$$2\pi \int_{2\sigma_0}^{r_0+a} g(R)(R-a)^2 \left(\frac{-4\sigma_0^2 + (r_0+a)^2}{2ar_0}\right) dR . \qquad \text{(D6)}$$

We must evaluate (D6) and then integrate over $d\vec{a}$. This is conveniently done by assuming that in the range of $2r_0 > R > 2\sigma_0$, $g(R)$ varies linearly with R, that is

$$g(R) = \bar{g}(R - 2\sigma_0) . \qquad \text{(D7)}$$

Equation (D7) is a good approximation for argon and also for hard spheres. Equation (D7) may be now substituted in (D6) and the integral over R performed. The resulting integral over a may now be evaluated but the result is too complex to present here. For argon $r_0 = 1.12\sigma_0$ and $P_d \cong 0.022$ at 84 °K. Hence $S^{\text{comm}}/k = 0.180$. This result is somewhat larger than that found in Sec. III A for argon by subtraction of two relatively large numbers but is nearly equal to that determined by machine for hard spheres (Sec. V).

---

*Based on work performed under the auspices of the U. S. Energy Research and Development Administration.

[1] (a) P. L. Fehder, J. Chem. Phys. 50, 2617 (1969); (b) P. L. Fehder, C. A. Emeis, and R. P. Futrelle, J. Chem. Phys. 54, 4921 (1971).

[2] (a) A. Rahman, Phys. Rev. 136, A405 (1964); (b) A. Rahman, J. Chem. Phys. 45, 2585 (1966).

[3] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. 150, 703 (1966).

[4] D. G. Henshaw, Phys. Rev. 105, 976 (1957); B. A. Dasannacharya and K. R. Rao, Phys. Rev. 137, A417 (1965).

[5] G. I. Distler and V. V. Moskvin, Zh. Eskp. Teor. Fiz. Pis. Red. 20, 551 (1974) [Sov. Phys. - JETP Lett. 20, 251 (1974)].

[6] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford, London, 1938), p. 638.

[7] F. H. Ree, in *Physical Chemistry, An Advanced Treatise,* edited by D. Henderson (Academic, New York, 1971), Vol. VIII A.

[8] P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, New York, 1967), pp. 60–63.

[9] W. J. Moore, *Physical Chemistry* (Prentice-Hall, New York, 1950).

[10] J. Kuebler and M. P. Tosi, Phys. Rev. 137, A1617 (1965).

[11] A. L. Gosman, R. D. McCarty, and J. G. Hust, National Standard Reference Data Series—National Bureau of Standards Report No. 27 (1969).

[12] D. E. O'Reilly and E. M. Peterson, J. Chem. Phys. 56, 5536 (1972).

[13] D. E. O'Reilly and E. M. Peterson, J. Chem. Phys. 55, 2155 (1971).

[14] (a) J. E. Lennard-Jones and A. F. Devonshire, Proc. R. Soc. (London) A169, 317 (1939); A170, 464 (1939); (b) H. Mori, S. Isa, H. Okamoto, and H. Furukawa, Prog. Theor. Phys. 48, 1474 (1972); T. Yoshida and H. Okamoto, *ibid.* 45, 663 (1971); T. Yoshida and K. Kamakura, *ibid.* 47, 1801 (1972); (c) T. Horiguchi and T. Tanaka, Phys. Rev. A 7, 1723 (1973); (d) D. Henderson and J. A. Barker, Mol. Phys. 14, 587 (1968).

[15] (a) H. C. Longuet-Higgins and B. Widom, Mol. Phys. 8, 549 (1964); (b) R. K. Crawford, J. Chem. Phys. 60, 2169 (1974); (c) Y. Rosenfeld, J. Chem. Phys. 63, 2769 (1975).

[16] J. P. Hansen and L. Verlet, Phys. Rev. 184, 151 (1969).