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[1] W. S. Ament and G. T. Rado, Phys. Rev. 97, 1558 (1955).

[2] D. S. Rodbell, Suppl. J. Appl. Phys. 30, 187S (1959); D. S. Rodbell, in Growth and Perfection of Crystals (John Wiley & Sons, Inc., New York, 1958), p. 247.

[3] L. Landau and E. Lifshitz, Physik. Z. Sowjetunion 8, 153 (1935).

[4] G. T. Rado and J. R. Weertman, J. Phys. Chem. Solids 11, 315 (1959).

[5] M. I. Kaganov and J. Liu, Izvest. Akad. Nauk SSSR, Ser. Fiz. 25, 1375 (1961) [translation: Bull. Acad. Sci. USSR, Phys. Ser. 25, 1388 (1961)].

[6] A. H. Mitchell, Phys. Rev. 105, 1439 (1957).

[7] I am grateful to T. W. Moore for providing his equipment for this measurement.

NATURE OF THE CRYSTALLINE SOLID AT ELEVATED TEMPERATURES

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We wish to report on some calculations performed in connection with the theory of melting developed by one of us (R.B.).[1] These calculations have not yet been completed to the point where they give the melting-point curve. We feel, however, that the results on the solid state are of sufficient interest to be made available immediately. Our findings indicate that considerable modification of the qualitative physical picture of a molecular solid is necessary when the ratio of the temperature to the Debye temperature satisfies $(T/\theta_D) \gtrsim 0.4$.

A brief resumé of the theory given in I, as modified for this calculation, follows. The basic self-consistent equation of I is

$$\rho(r)=\frac{\exp[-\beta\int v(\vec{r}-\vec{r}\,')g_{\mathrm{HC}}(\vec{r}-\vec{r}\,')\rho(\vec{r}\,')d^3r']}{\int\exp[-\beta\int v(\vec{r}-\vec{r}\,')g_{\mathrm{HC}}(\vec{r}-\vec{r}\,')\rho(\vec{r}\,')d^3r']d^3r}. \quad (1)$$

Here $\rho(r)$ is the single-particle periodic density, $v(\vec{r}-\vec{r}\,')$ is the attractive part of the intermolecular potential, $\beta=(1/\kappa T)$, and $g_{\mathrm{HC}}(\vec{r})$ is the hard-core exclusion factor given by

$$\begin{aligned} g_{\mathrm{HC}}(r)&=1, \quad r>c,\\ &=0, \quad r>c, \end{aligned} \quad (2)$$

where c is the hard-core diameter. Any periodic function may be written as

$$\rho(\vec{r})=\sum_{\vec{R}i}\varphi(\vec{r}-\vec{R}i), \quad (3)$$

where $\vec{R}i$ are the lattice points. We assume that the solid is such that the particles are localized within their unit cells, and hence that in the ith cell only the ith member of the sum in Eq. (3) contributes significantly to $\rho(r)$. In that case, Eq. (1) reads

$$\varphi(\vec{r})=\exp[-\sum_{R\neq 0}\beta\int r(\vec{r}-\vec{r}\,')\varphi(\vec{r}-\vec{R})d^3r']\{\int_{\text{unit cell}}\exp[-\sum_{R\neq 0}\beta\int r(\vec{r}-\vec{r}\,')\varphi(\vec{r}\,'-\vec{R})d^3r']d^3r\}^{-1}. \quad (4)$$

The free energy (see I) is given by

$$-\frac{\beta F}{N}=-\int\varphi(\vec{r})\ln\varphi(\vec{r})d^3r-\left(\frac{\beta}{Z}\right)\sum_{R\neq 0}\int v(\vec{r}-\vec{r}\,')g_{\mathrm{HC}}(\vec{r}-\vec{r}\,')\varphi(\vec{r})\varphi(\vec{r}\,'-\vec{R})d^3r\,d^3r'. \quad (5)$$

The equilibrium distance, R_0, is determined as a function of T by minimizing F with respect to R_0. The external pressure is assumed negligible. To facilitate calculation we have replaced the summation over the 12 near neighbors by an integration over a spherical shell.

At low temperatures φ tends to the familiar Gaussian density about the equilibrium position. In fact, an expansion of the potential about the equilibrium sites in Eqs. (4) and (5) yields the Grüneisen equation of state based on the Einstein model. At higher temperatures it becomes important to make the theory self-consistent, i.e., to take into account modification in the effective cell potential arising from the oscillations of neighbors. These oscillations confront one with the problems of avoiding overlapping of hard cores. A self-consistent solution of Eq. (4) dictates that $\varphi(\vec{r}) = 0$ when r reaches a value such that the core edge overlaps the cell boundary. This idea receives confirmation upon comparing with Alder's calculations of the equation of state of a dense hard-core medium,[2] i.e., at densities characteristic of the solid. Here it was confirmed that the free-volume equation of state is an accurate approximation. When the attractive potential vanishes, our theory, as might be expected, goes over to the free-volume approximation.

To perform the calculations we have taken the intermolecular potential to be of the Lennard-Jones variety for $r > c$, c = the hard-core diameter:

$$\begin{aligned} v(r) &= 4\epsilon[(c/r)^{12} - (c/r)^6], \quad r > c, \\ &= \infty, \quad r < c. \end{aligned} \tag{6}$$

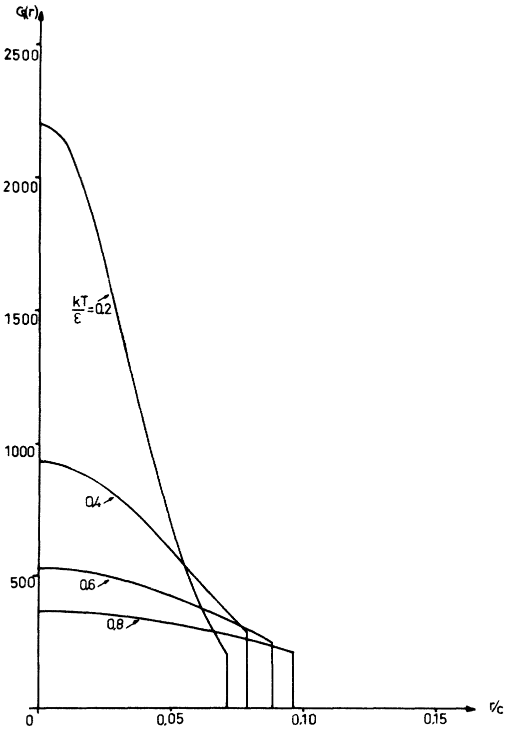

FIG. 1. Normalized distributions $\varphi(r)$ at varying temperature. The melting point is at $(kT/\epsilon) = 0.67$.

Here ϵ is the potential minimum. Our working substance is argon, for which $\epsilon = 120°\mathrm{K}$, and $c = 3.4$ Å.[3] This potential is very approximate, and our calculation will necessarily be of limited accuracy because of our ignorance of the details of the potential.

The solution of Eq. (4) was carried out by iteration beginning with a Gaussian form for $\varphi(r)$. This was done on an IBM electronic computer. R_0 was chosen by picking the minima of a series of calculated values of F. The results for these normalized distributions $\varphi(r)$ at various temperatures are given in Fig. 1, and the equilibrium interparticle distance as a function of T is given in Fig. 2. Experimentally, the melting point of argon is at $(\kappa T/\epsilon) = 0.67$. We remark that the equilibrium distance R_0 at the melting point is calculated to be $(1.185c)$, as compared to the experimental value of $(1.18) \times 3.4$ Å. Thus, agreement with experiment is good. The thermal expansion coefficient in the vicinity of 60°K is calculated to be about 0.23 %/°K, as against the experimental value of 0.19 %/°K. For comparison, in Fig. 2 we have drawn in the Grüneisen-Einstein result, which, as is well known, gives an instability somewhat ahead of the melting point.[3]

Our first point in the discussion of these results is that the thermal expansion in our self-consistent theory is indeed approximately linear up to the melting point. Instability ensues somewhat above. Next, in Fig. 1 one sees that for $(\kappa T/\epsilon) \lesssim 0.5$ the distribution still has a concentra-

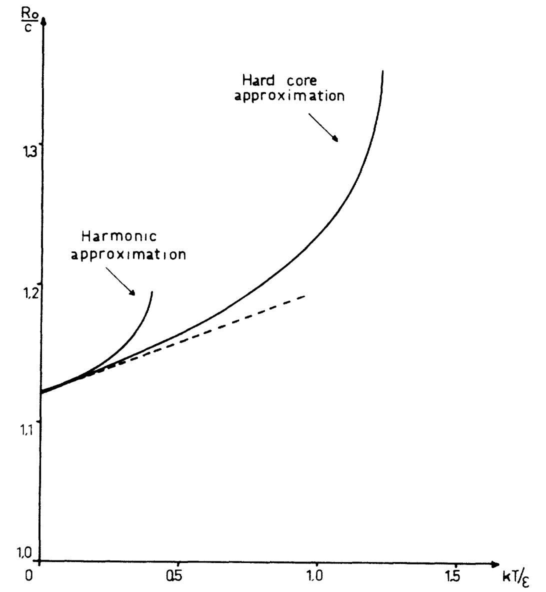

FIG. 2. Calculated plots of the equilibrium interparticle distance as a function of T. c is the hard-core diameter.

tion of probability at the cell center, whereas for higher temperatures the distribution indeed becomes flat, characteristic of the free-volume theory. Our main finding is, then, that as a solid approaches its melting temperature it already has acquired somewhat the character of a cell-model liquid. Under these conditions the energy of the solid can only be slightly lower than the energy of a hypothetical liquid at the same density, whereas the entropy is much less because of the imposed periodicity. We are approaching melting. We will publish further details of this calculation when we have completed work on the equation of state of the liquid. The latter involves other considerations then those described above. At that time we hope to present a melting curve.

The theory here presented requires modification on two scores. Firstly, quantum effects will certainly be important so long as there is considerable concentration of the distribution near the cell center, $(\kappa T/\epsilon) \lesssim 0.5$. At low temperatures, zero-point pressure is already functioning in the expansion process. We therefore expect that the quantum effects will reduce the expansion coefficient in line with experiment. The second deficiency is our neglect of the long-wavelength correlations (phonons). We think that these collective effects will not bear great weight. This is because in the melting region all phonons are excited, and those with short wavelength fill most of the Brillouin zone.

We are presently concerned with the quantitative treatment of these deficiencies. There have been a number of careful quantum-mechanical treatments of the problem.[4,5] However, these have not been self-consistent, and they have relied on perturbation theory in treating the intrinsically anharmonic character of the intermolecular potential. We think it premature to make quantitative comparison with these calculations, but hope to return to this problem in future work.

Note added in proof.–Since our Letter was submitted, we have performed a more thorough calculation of density as a function of temperature at zero pressure. The zero-pressure approximation is valid for $p \ll p_{\text{internal}} \simeq 10^3$ atmospheres. Our new calculation has included the effects of more distant neighbors. The distributions, $\varphi(r)$, remain the same. We find, with $c = 3.4$ Å, perfect agreement between calculated and experimental density for $0.4 \lesssim (\kappa T/\epsilon_0) \lesssim 0.7$. The upper limit is the melting region. Presumably, agreement extends into the metastable solid. At lower temperatures the calculated density is too high; the maximum deviation of ~4% occurs at $T = 0$. These deviations are presumed to be quantum and phonon effects, which we are currently working out. We also plan to extend our calculations to finite pressure; however, this will only affect our results about and above 10^3 atm. Our principal result, the flatness of $\varphi(r)$ in the normal melting region, will therefore not be affected by these further calculations.

We have also made an initial estimate of the melting point at low pressure. Our model for the liquid was to take the entropy to be that of a hard-core gas and the energy to be that of the attractive tail in a hard-core medium. We thus neglect the decrease in entropy due to local order induced by the attraction. The calculated melting point is 25% too low. We attribute the deviation to errors in the liquid model, since the solid agrees so well with experiment. The sign of the deviation is correct and a 25% decrease in the liquid entropy would probably set things right. We are presently engaged in a study of this problem.

We anticipate publishing a complete account of our program at some future date.

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[1] R. Brout, Physica 29, 1041 (1963); this paper will be referred to as I. (The rather new approach to the statistical mechanics of crystalline solids employed in I and in the present paper is reviewed in detail by R. Brout, to be published.)

[2] B. J. Alder and T. E. Wainwright, Phys. Rev. 127, 359 (1962).

[3] E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. 20, 516 (1957).

[4] C. Domb and I. J. Zucker, Nature 178, 484 (1956).

[5] E. A. Guggenheim and M. L. McGlasham, Proc. Roy. Soc. (London) A255, 456 (1960).