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Abstract

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On the Theory of Melting

(Presented by Academician N. N. Bogolyubov, 9 VII 1960)

The existing methods for determining the binary distribution function for a liquid have not so far led to the construction of a satisfactory statistical theory of crystallization. In the present note we indicate another way of finding the crystallization temperature and the thermodynamic functions of a crystal near the transition point, approaching this point not from the side of the disordered (liquid) phase, but from the side of the crystal. In doing so we shall use the variational principle of N. N. Bogolyubov and shall start at first from the simplest Einstein model of a crystal as an assembly of particles oscillating independently of one another about their equilibrium positions with one and the same frequency ω. As the temperature is raised, the frequency of these oscillations will change and, beginning from some temperature T_{m}, will vanish altogether: the crystal will begin to melt, and the temperature T_{m} is its melting temperature.

Let the interaction energy of two atoms of a crystal situated at a distance r' be equal to $\Phi(r')$. Then the interaction energy of a mole of crystal will be

$$U = \sum_{1 \leq i < k \leq N} \Phi\left(r'_{ik}\right) \tag{1}$$

(N is Avogadro' s number).

We divide the energy U into two parts U_0 and U_1. According to Bogolyubov' s variational principle, the free energy of the crystal is determined by the expression

$$F \leq F_0 + \langle U_1 \rangle, \tag{2}$$

where F_0 is the free energy corresponding to the energy U_0, and $\langle U_1 \rangle$ is the value of the energy U_1 averaged with respect to U_0. Let U_0 be the energy of harmonically oscillating atoms with frequency ω:

$$U_0 = \sum_{(N)} u_0, \qquad u_0 = \begin{cases} \frac{1}{2} m\omega^2 r^2, & r < b; \\ \infty, & r > b \end{cases}$$

Fig. 1

Figure 1: Fig. 1

(m, u_0, b are respectively the mass, the energy, and the size of the region of oscillation of the atom).

Consider a crystal in which the number of nearest neighbors (coordination number) of each atom is equal to z, and take into account the interaction of atoms only with their nearest neighbors. Then

$$\langle U_1\rangle = \left\langle \sum \Phi\left(r'_{ik}\right) - U_0 \right\rangle = \sum \langle \Phi\left(r'_{ik}\right) - u_0\rangle = \tfrac{1}{2} zN \langle \Phi(r')\rangle - N\langle u_0\rangle. \quad (3)$$

For inert-gas crystals having a face-centered cubic structure ($z = 12$), the Lennard-Jones potential may be taken for $\Phi(r)$:

$$\Phi(r') = \begin{cases} \infty, & r < \sigma; \\ 4u\left[\left(\dfrac{\sigma}{r'}\right)^{12} - \left(\dfrac{\sigma}{r'}\right)^{6}\right], & r > \sigma, \end{cases} \quad (4)$$

where u and σ are two parameters (respectively of the dimensions of energy and length), determining the magnitude of the intermolecular force and varying from substance to substance.

The minimum of $\Phi(r')$ is equal to u and occurs at $r' = a = \sigma\sqrt[6]{2}$,

$$\langle \Phi(r')\rangle = \left[\int_0^{\pi}\int_0^{b} \Phi(r') e^{-\alpha r^2} r^2 \sin\varphi \, d\varphi \, dr\right] \Big/ \left[2\int_0^{b} e^{-\alpha r^2} r^2 \, dr\right], \quad (5)$$

where $b = (\sqrt[6]{2} - 1)\sigma$, $\alpha = m'\omega^2/2\theta = m\omega^2/4\theta$ ($m' = m/2$ is the reduced mass of the oscillating atom M; $\theta = kT$; k is Boltzmann' s constant; T is the absolute temperature; φ is the polar angle (see Fig. 1), a is the lattice constant).

Since $r' = \sqrt{r^2 + a^2 - 2ar\cos\varphi}$, for the potential (4) we obtain

Fig. 1

$$\langle \Phi(r')\rangle = \frac{\omega^3}{\theta\sqrt{\theta}} A \int_0^{b} B(r) e^{-m\omega^2 r^2/4\theta} r \, dr, \quad (6)$$

where

$$A = \frac{u\sigma^2 m}{2a}\sqrt{\frac{m}{\pi}}; \quad (7)$$

$$B(r) = \frac{\sigma^{10}}{5}\left[(r-a)^{-10} - (r+a)^{-10}\right] - \frac{\sigma^4}{2}\left[(r-a)^{-4} - (r+a)^{-4}\right]. \qquad (8)$$

In the classical case

$$F_0 = -3N\theta \ln \frac{\omega}{\theta}, \qquad \langle u_0 \rangle = {}^3/_2\theta \qquad (9)$$

(when calculating $\langle u_0 \rangle$, the upper limit in integrals of the form $\int_0^b e^{-\alpha r^2}\, dr$ is replaced by ∞).

Substituting (6) and (9) into (2), we shall have:

$$F \leq -3N\theta \ln \frac{\omega}{\theta} + \frac{zN\omega^3}{2\theta\sqrt{\theta}}\, A \int_0^b B(r) e^{-m\omega^2 r^2/4\theta} r\, dr - \frac{3}{2}\theta. \qquad (10)$$

Equation (10) determines an upper bound for the free energy and is a function of the energy-partition parameter—the frequency ω. The best estimate of the free energy is obtained when this parameter is determined from the condition for a minimum of the upper bound of the free energy, $\partial F/\partial\omega = 0$, which leads to the equation

$$1 + \frac{3um\sigma^2\omega^3}{a\theta^2}\sqrt{\frac{m}{\pi\theta}} \int_0^b B(r) e^{-m\omega^2 r^2/4\theta} r\, dr -$$

$$-\frac{u\sigma^2 m^2 \omega^5}{2a\theta^3}\sqrt{\frac{m}{\pi\theta}} \int_0^b B(r) e^{-m\omega^2 r^2/4\theta} r^3\, dr = 0. \qquad (11)$$

This is the fundamental equation of the theory of melting—it determines the melting temperature T_m and makes it possible to find the free energy of the crystal near the transition point.

The dependence of the frequency (more precisely, $y = 10^{-11}\omega$) on the temperature T, as determined by equation (11), has the form shown in Fig. 2. The melting temperature T_m corresponds to the value of T in equation (11) starting from which the solution for ω disappears.

The numerical solution of equation (11) for crystals of the inert gases Ar, Ne, Kr, and Xe leads to values of T_m exceeding the experimental melting temperatures $T_\mathrm{m}^\mathrm{exp}$ of these crystals; however, the ratio $T_\mathrm{m}/T_\mathrm{m}^\mathrm{exp}$ is the same for all four gases and is approximately equal to 3. Thus, if, on the basis of the result for some one crystal (for example, Ar), the temperature scale in (11) is changed (reduced by a factor of 3), then in all the remaining cases (crystals of Ne, Kr, and Xe) we shall obtain from (11) melting temperatures exactly equal to the experimental ones.

Fig. 2

Figure 2: Fig. 2

Fig. 2

The difference between the values of T_{m} given by equation (11) and the experimental melting temperatures $T_{\text{m}}^{\text{exp}}$ is explained mainly by the crudeness of the Einstein crystal model used. We hope that, along the path proposed in the present article, the agreement between T_{m} and $T_{\text{m}}^{\text{exp}}$ can be improved by a more rigorous approach to the problem.

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Note: Figure translations are in progress. See original paper for figures.