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Abstract

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E. A. ARINSHTEIN

THE PHENOMENON OF CRYSTALLIZATION IN STATISTICAL PHYSICS

(Presented by Academician N. N. Bogolyubov, 25 X 1956)

The problem of crystallization in statistical physics has not yet been solved. The method of A. A. Vlasov ([1]) always leads to continuous crystallization. It is difficult to determine the accuracy of his equations and the form of the kernel. Similar results were obtained by S. V. Tyablikov ([2]). He proceeds from an arbitrary representation of the binary function in terms of unary ones. Kirkwood ([3]) proceeds from the same representation. Moreover, the kernel of Kirkwood' s equation cannot be determined either theoretically or experimentally. Nor is the problem solved by works in which either only the liquid ([4]) or only the crystalline phase ([5,6]) is considered, or by works based on model representations ([7,8]).

In the present work crystallization is investigated by the method of N. N. Bogolyubov ([9]), which makes it possible to relate thermodynamic functions to the structure.

We define the distribution function of s particles through the generating functional:

$$F_s(1\dots s) = V^s \int D_N dq_{s+1}\dots dq_N = \left[\frac{\delta^s L(u)}{\delta u(1)\dots\delta u(s)}\right]_{u=0};$$

$$L(u) = \int D_N \prod_{i=1}^{N}(1+vu(i))\,dq_i. \tag{1}$$

The functional $W(u) = \ln L$ determines the correlation functions:

$$g_s = \left[\frac{\delta^s W(u)}{\delta u(1)\dots\delta u(s)}\right]_{u=0}; \qquad F_1 = g_1; \quad F_2(1,2) = F_1(1)F_1(2) + g_2(1,2);\dots \tag{2}$$

We shall use the functional equation of N. N. Bogolyubov:

$$\frac{\delta^s L(u)}{\delta u(1)\dots\delta u(s)} = (zv)^s \exp\left(-\frac{U_s}{\vartheta}\right) L\left(u(i)(\varphi_{1\dots s}(i)+1)+\frac{1}{v}\varphi_{1\dots s}(i)\right), \qquad (3)$$

where

$$\varphi_{1\dots s}(i) = \prod_{j=1}^{s}(1+f_{ij}) - 1 \quad (i>s); \qquad f_{ij} = \exp\left(-\frac{U_{ij}}{\vartheta}\right) - 1$$

and z is the activity. Taking the logarithm and then the functional derivative of (3), we obtain, for $s = 1$:

$$\frac{\delta^2 W(u)}{\delta u(1)\delta u(2)} = \frac{\delta W(u)}{\delta u(1)}\left\{\frac{\delta W\left(u(i)(1+f_{1i})+\frac{1}{v}f_{1i}\right)}{\delta u(2)} - \frac{\delta W(u)}{\delta u(2)}\right\}. \qquad (4)$$

By further functional differentiation and substitutions, all g_s can be expressed through F_1 in any approximation with respect to correlations, i.e., with accuracy up to any term in the expansion of the functional $W(u)$.

For the distribution function F_1, this method gives the equation:

$$\ln\frac{F_1(1)}{zv} = \sum_{s=1}^{\infty}\frac{1}{v^s s!}\int K_{s+1}(1,\dots,s+1)F_1(2)\dots F_1(s+1)\,dq_2\dots dq_{s+1} = W\left(\frac{1}{v}f_{1i}\right), \qquad (5)$$

where

$$K_2(1,2) = f_{12}; \qquad K_3(1,2,3) = f_{12}f_{13}f_{23}; \dots$$

For $F_1 \equiv 1$, the system of correlation approximations coincides with the expansion in powers of the density. But (5) also has a periodic solution, which cannot be obtained by an expansion in powers of the density. Equation (5), with the additional normalization condition $\langle F_1\rangle_{\text{cp}} = 1$, is equivalent to the problem of finding the conditional extremum of the functional

$$A(F_1, v, \vartheta) = \vartheta\left\langle F_1(1)\ln F_1(1) - \sum_{s=1}^{\infty}\frac{F_1(1)}{v^s(s+1)!}\int K_{s+1}(1,\dots,s+1)\,F_1(2)\dots \right.$$
$$\left.\dots F_1(s+1)\,dq_2\dots dq_{s+1}\right\rangle_{\text{cp}} - \vartheta\ln\frac{v(2\pi m\vartheta)^{3/2}}{h^3}, \qquad (6)$$

determined from (5) to within terms and factors that do not depend on F_1. They are chosen so that $A(F_1)$ is equal to the specific free energy. Indeed, at constant temperature and density the equilibrium distribution corresponds to the minimum of the free energy. We shall prove, moreover, that the pressure and internal energy are expressed through the derivatives of the functional A with respect to v and ϑ. The pressure, according to ([9]), is equal to

$$p = \frac{\vartheta}{v}\left\{1 - \frac{1}{6\vartheta}\left\langle \int \frac{du(\lambda r_{12})}{d\lambda}\Big|_{\lambda=1} F_2(1,2)\, dq_2 \right\rangle_{\text{cp}}\right\}. \tag{7}$$

We express F_2 with the aid of (4). For this purpose, in (5) we replace f_{1i} by $f_{1i}+vu(i)(1+f_{1i})$, while the f_{ij} not containing the coordinate (1) are not transformed, and take the functional derivative. After a number of transformations we obtain

$$F_2(1,2) = F_1(1)F_1(2)(1+f_{12})\sum_{s=1}^{\infty}\frac{1}{v^{s-1}(s-1)!}\int \frac{\partial K_{s+1}(1,\dots,s+1)}{\partial f_{12}} F_1(3)\dots F_1(s+1)\, dq_3 \dots dq_{s+1}, \tag{8}$$

$$p = \frac{\vartheta}{v}\left\{1 - \sum_{s=1}^{\infty}\frac{1}{v^s(s+1)!}\left\langle \int K_{s+1}(1,\dots,s+1)\left[\left(s - \frac{1}{3}\frac{d}{d\lambda}\right)F_1\left(\frac{r_1}{\lambda}\right)\dots \right.\right.\right.$$
$$\left.\left.\left. \dots F_1\left(\frac{r_{s+1}}{\lambda}\right)\right]\right]_{\lambda=1} dq_2 \dots dq_{s+1}\right\rangle_{\text{cp}}\Bigg\}. \tag{9}$$

$$F_1 = \sum a_l \exp[i(k_l r)],$$

where $k_l = 2\pi b_l$, and b_l are vectors of the reciprocal lattice, and $\partial A/\partial a_l = 0$. Under uniform compression, $k_l \sim v^{-1/3}$;

$$\frac{1}{3}\frac{d}{d\lambda}F_1\left(\frac{r}{\lambda}\right)\Big|_{\lambda=1} = -\frac{1}{3}\sum_l \left(k_l \frac{\partial F_1}{\partial k_l}\right)_{a_l} = \left(v\frac{dF_1}{dv}\right)_{a_l},$$

and $p = -\partial A/\partial v$.

The expression for the internal energy (see ([9])) is easily reduced, with the aid of (8), to the form $-\vartheta^2\partial(A/\vartheta)/\partial\vartheta$. The constants contained in the last term of expression (6) are determined by comparison with the expansion in powers of the density and, generally speaking, are inessential. Thus, the functional (6) expresses the relation between the structure and the thermodynamic functions.

The deviation of the particles from their equilibrium positions in a crystal is the sum of a large number of random variables and, consequently, the distribution is

distributed according to a normal law. For structures with high symmetry this distribution is spherically symmetric, and the function F_1 can be specified in the form

$$F_1 = \frac{v}{(2\pi)^{3/2} r_0^3} \sum_l \exp\left\{-\frac{(\mathbf{r}-\mathbf{r}_l)^2}{2r_0^2}\right\} = \sum_l \exp\left\{-\frac{r_0^2 k_l^2}{2} + i(\mathbf{k}_l \mathbf{r})\right\}. \quad (10)$$

The width of the distribution r_0 is the only variational parameter, determined from the condition $\partial A(r_0)/\partial r_0 = 0$.

For small values of r_0 the function $(2\pi)^{-3/2} r_0^{-3} \exp(-r^2/2r_0^2)$ has a δ-like character, and, expanding the kernels K near the lattice sites, we obtain:

$$A = -\frac{3}{2}\vartheta - \vartheta \ln \frac{(m\vartheta)^{3/2} r_0^3}{h^3} - \vartheta \sum_{s=1}^{\infty} \frac{1}{s!} \sum_{l_1 \ldots l_s} K_{s+1}(0, \mathbf{r}_{l_1}, \ldots, \mathbf{r}_{l_s}) + O(r_0^2), \quad (11)$$

whence it follows that $\partial A/\partial r_0 = -3\vartheta/r_0 + O(r_0) < 0$.

In the case of large r_0 we shall use the expansion (10) of the function F_1 in a Fourier series. If for large r_0, $\partial A/\partial r_0 > 0$, then the functional $A(F_1)$ has a minimum at a finite value of r_0; otherwise a periodic structure may be absent. Direct substitution of (10) into (6) gives:

$$\begin{aligned} A(r_0, \vartheta, v) = &-\vartheta \ln \frac{v(2\pi m\vartheta)^{3/2}}{h^3} - \vartheta \sum_{s=1}^{\infty} \frac{K_{s+1}}{v^s (s+1)!} \\ &- \frac{\vartheta}{2!} {\sum_l}' \exp[-k_l^2 r_0^2]\{\sigma(\mathbf{k}_l) - 1\} \\ &- \frac{\vartheta}{3!} {\sum_{\mathbf{k}_{l_1}+\mathbf{k}_{l_2} \neq 0}}'' \exp\left[-\frac{(\mathbf{k}_{l_1}+\mathbf{k}_{l_2})^2 + k_{l_1}^2 + k_{l_2}^2}{2} r_0^2\right] \{\sigma(\mathbf{k}_{l_1}, \mathbf{k}_{l_2}) - 1\} - \ldots, \end{aligned} \quad (12)$$

$$\frac{\partial A}{\partial r_0} = \vartheta r_0 \Bigg\{ \sum{}' k_l^2 \exp[-k_l^2 r_0^2]\{\sigma(\mathbf{k}_l) - 1\} + \frac{1}{3} \sum_{\mathbf{k}_{l_1}+\mathbf{k}_{l_2}\neq 0}{}'' \frac{(\mathbf{k}_{l_1}+\mathbf{k}_{l_2})^2 + k_{l_1}^2 + k_{l_2}^2}{2} \exp\left[-\frac{(\mathbf{k}_{l_1}+\mathbf{k}_{l_2})^2 + k_{l_1}^2 + k_{l_2}^2}{2} r_0^2\right] \times \{\sigma(\mathbf{k}_{l_1}, \mathbf{k}_{l_2}) + 1\} + \ldots \Bigg\}, \tag{13}$$

where

$$K_{s+1} = \int K_{s+1}(1, \ldots, s+1)\, dq_2 \ldots dq_{s+1}; \qquad \sigma(\mathbf{k}_l) = \frac{1}{v} \int \exp[i(\mathbf{k}_l \mathbf{r})] K(\mathbf{r})\, dq_2;$$

$$K(\mathbf{r}) = \sum_{s=1}^{\infty} \frac{1}{v^{s-1}(s-1)!} \int K_{s+1}(1, \ldots, s+1)\, dq_3 \ldots dq_{s+1};$$

$$\sigma(\mathbf{k}_{l_1}, \mathbf{k}_{l_2}) = \frac{1}{v^2} \int \exp[i(\mathbf{k}_{l_1} \mathbf{r}_{12}) + i(\mathbf{k}_{l_2} \mathbf{r}_{13})] K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, dq_2 dq_3;$$

$$K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_{s=2}^{\infty} \frac{1}{v^{s-2}(s-2)!} \int K_{s+1}(1, \ldots, s+1)\, dq_4 \ldots dq_{s+1}.$$

The sign of $\partial A / \partial r_0$ for large r_0 is determined by the sign of the principal term, and the condition for the existence of a periodic solution takes the form:

$$\sigma(\mathbf{k}) = \frac{4\pi}{v} \int_0^{\infty} K(r) \frac{\sin kr}{kr} r^2 dr > 1. \tag{14}$$

The region of thermodynamically stable crystalline states is determined by the conditions:

$$\frac{\partial A}{\partial r_0} = 0; \qquad p_{\text{cr}}(v_{\text{cr}}, \vartheta) = p_{\text{tv}}(v_{\text{tv}}, \vartheta); \qquad \mu_{\text{cr}}(v_{\text{cr}}, \vartheta) \geq \mu_{\text{tv}}(v_{\text{tv}}, \vartheta). \tag{15}$$

For given v_{tv} and ϑ, the first of conditions (15) determines the value of r_0, and the second determines v_{cr}. For small $\Delta v = v_{\text{cr}} - v_{\text{tv}}$, one can eliminate Δv and, taking into account the first of equations (15) and the expansion (13), obtain the stability condition in the form:

$$\sum_l{}' \exp[-k_l^2 r_0^2]\{\sigma(\mathbf{k}_l)-1\}+\frac{1}{3}\sum_{\mathbf{k}_{l_1}+\mathbf{k}_{l_2}\neq 0}{}'' \exp\left[-\frac{(\mathbf{k}_{l_1}+\mathbf{k}_{l_2})^2+k_{l_1}^2+k_{l_2}^2}{2}\,r_0^2\right]\{\sigma(\mathbf{k}_{l_1},\mathbf{k}_{l_2})+1\}+\ldots\geq 0. \tag{16}$$

For example, for a face-centered cubic lattice the stability region and the parameter r_0 are determined by the following conditions:

$$\sigma(\mathbf{k})-1+\exp\left[-\frac{k^2r_0^2}{3}\right]\left[\sigma\left(\frac{2k}{\sqrt{3}}\right)-1\right]+5\exp\left[-\frac{2k^2r_0^2}{3}\right][\sigma(\mathbf{k},\mathbf{k})+1]+\ldots=0, \tag{17}$$

$$\left[\sigma\left(\frac{2k}{\sqrt{3}}\right)-1\right]+8\exp\left[-\frac{k^2r_0^2}{3}\right][\sigma(\mathbf{k},\mathbf{k})+1]+\ldots\leq 0, \tag{18}$$

where $\mathbf{k}$ is the principal vector of the reciprocal lattice (multiplied by 2π), and $v=6\sqrt{3}\pi^3/k^3$. To determine all properties of the crystal, the equation of state (9) should be added to equations (17) and (18).

From the system (17), (18) follows the possibility of continuous crystallization. The line of the continuous transition is determined by the equation

$$\sigma(k)\equiv\frac{4\pi}{v}\int_0^\infty K(r)\frac{\sin kr}{kr}\,r^2dr=1 \tag{19}$$

under the condition $\sigma(2k/\sqrt{3})<1$. For $\sigma(2k/\sqrt{3})>1$, crystallization will be a first-order transition with a jump in density; the transition line is determined by the system (17), (18), if in (18) the sign $\leq$ is replaced by the equality sign.

Calculations carried out for the simplest model of interaction (an infinite barrier and a narrow well) in the first and second approximations with respect to correlations showed that at high temperatures there are no periodic solutions; then there follows a region of continuous crystallization, and only at lower temperatures does crystallization become a first-order transition.

In the work of L. D. Landau[10] it is asserted that crystallization can be continuous only at isolated points. This conclusion follows from the assumption that the Fourier series of the function F_1 contains only one harmonic. However, in the expansion (10) all harmonics are present, with coefficients that are small quantities of higher orders. A region of continuous crystallization was also obtained by Lennard-Jones and Devonshire[8] by the free-volume method.

In the first approximation with respect to correlations, equation (5) coincides with the equations of A. A. Vlasov and S. V. Tyablikov. In the following approximations the kernel, determined in the work[2], turns out to be inexact.

Tomsk Engineering-Construction Institute

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