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STATISTICAL THEORY OF STRUCTURAL AND THERMODYNAMIC

PROPERTIES OF MOLECULAR CRYSTALS

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UDC 539.3

A crystal theory is constructed on the basis of the statistical method of conditional distributions. A closure procedure is suggested, making it possible to take into account the correlation of various orders, and several structural and thermodynamic quantities are calculated

Along with the traditional approach of describing the crystalline structure of matter, based on Born's ideas [1], several variations of the statistical theory of crystals have been actively pursued lately, based on the apparatus of particle distribution functions [2-7]. The latter tendency is particularly due to the trend of characterizing the high-temperature region of the crystalline phase, as well as due to the fact that, unlike the theory of lattice dynamics, the distribution function formalism is applicable, in principle, to all phases of matter, thus creating the prerequisites for describing the region of the crystal-disordered phase transition.

The biggest difficulty of this approach is associated with the necessity of developing a closure procedure, without destroying the validity of the original equations in relation to any phase. This closure was suggested within the statistical method of conditional distributions [8]. It was based on the approximation of integral terms, having the meaning of average force potentials, and allowed to provide a unified description of all first-order phase transitions [9].

It was shown within this closure [7] that, retaining the general features of the approach, one can construct for the crystalline phase an analytic theory making it possible to calculate a wide set of crystal characteristics.

Based on a modified closure procedure [10] and physical ideas used in [7], in the present paper we construct a statistical theory of molecular crystals with central pair interactions.

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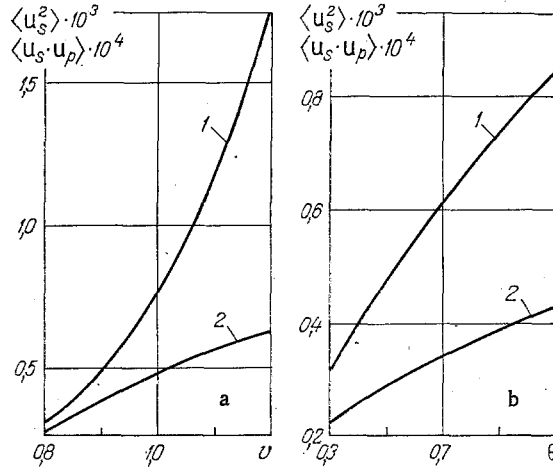


Fig. 1. The mean-square displacement $\langle u_s^2 \rangle \cdot 10^3$ (1) and the pair correlator $\langle u_s \cdot u_p \rangle \cdot 10^4$ (2) as a function of molecular volume ($\theta = 0.7$) (a) and of temperature ($v = 0.95$) (b).

Consider a system of N particles in a volume V , divided into N cells $v_i = V/N$. To describe the crystal we use distribution functions $F(s)$, $F(s, p)$, $F(s, p, t)$ [8], determining the probability densities of finding, respectively, one, two, and three particles near the points $q_s \in v_s$, $q_p \in v_p$, and $q_t \in v_t$, under the condition that in the remaining molecular cells $v_i (i = s, p, t)$ there is one particle. These functions satisfy the following system of integrodifferential equations:

$$\nabla_s [\ln F(s) + \beta \varphi_s] = 0, \quad (1)$$

$$\nabla_s [\ln F(s, p) + \beta (\Phi_{sp} + \varphi_{sp})] = 0, \quad (2)$$

$$\nabla_s [\ln F(s, p, t) + \beta (\Phi_{sp} + \Phi_{st} + \varphi_{spt})] = 0, \quad (3)$$

whose formal solutions are

$$F(s) = c_s \exp(-\beta \varphi_s), \quad (4)$$

$$F(s, p) = c_{sp} \exp[-\beta (\Phi_{sp} + \varphi_{sp})], \quad (5)$$

$$F(s, p, t) = c_{spt} \exp[-\beta (\Phi_{sp} + \Phi_{st} + \varphi_{spt})]. \quad (6)$$

The quantities φ_s , φ_{sp} , and φ_{spt} have the meaning of average potential forces acting on a given particle by the whole surrounding except particles with subscripts s , s and p , and s , p , and t , respectively. They are determined as follows:

$$\varphi_s = \sum_{i \neq s}^N \varphi_{s,i}; \quad \varphi_{sp} = \sum_{i \neq s,p}^N \varphi_{sp,i}; \quad \varphi_{spt} = \sum_{i \neq s,p,t}^N \varphi_{spt,i}. \quad (7)$$

The average forces are determined by the expressions:

$$\nabla_s \varphi_{s,i} = \int_{v_i} \nabla_s \Phi_{si} [F(s, i)/F(s)] d(i), \quad (8)$$

$$\nabla_s \varphi_{sp,i} = \int_{v_i} \nabla_s \Phi_{si} [F(s, p, i)/F(s, p)] d(i), \quad (9)$$

$$\nabla_s \varphi_{spt,i} = \int_{v_i} \nabla_s \Phi_{si} [F(s, p, t, i)/F(s, p, t)] d(i). \quad (10)$$

As a preliminary step toward closing the chain (1)-(3) (or, which is the same, (4)-(6)) we represent the normalization coefficients of the functions (5) and (6) in the form

$$c_{sp} = c_s c_p \lambda_{sp}, \quad c_{spt} = c_s c_p c_t \lambda_{spt}, \quad (11)$$

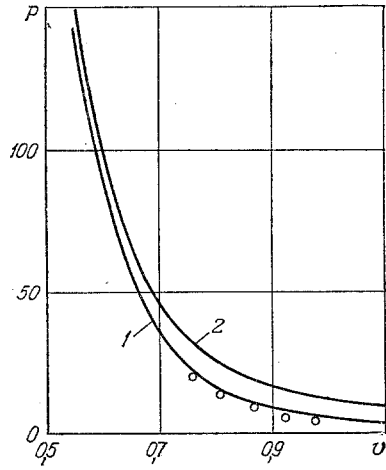


Fig. 2

Fig. 2. Pressure as a function of molecular volume and temperature: 1) $\theta = 0.3$; 2) $\theta = 0.8$, the points are the experimental values of [15]. P , kbar.

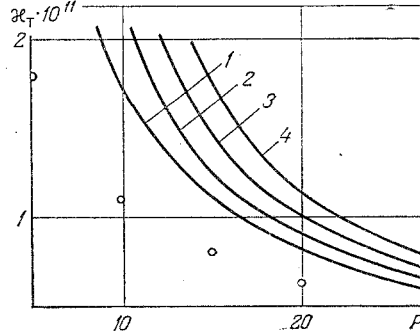


Fig. 3

Fig. 3. Isothermal compressibility as a function of temperature and pressure: 1) $\theta = 0.3$; 2) 0.4; 3) 0.5; 4) 0.6, the points are experimental values [16].

where λ are new coefficients, concerning which it is sufficient to state that they are positive, and any of the coefficients c_i is determined from the normalization condition of the single-particle function (4):

$$c_i^{-1} = \int_{v_i} \exp(-\beta\varphi_i) d(i). \quad (12)$$

We introduce now new average force potentials

$$\psi_{sp} = \varphi_{sp} - \beta^{-1} \ln \lambda_{sp}, \quad \psi_{spt} = \varphi_{spt} - \beta^{-1} \ln \lambda_{spt}, \quad (13)$$

each of which is determined by a sum of form (7), with

$$\nabla_s \varphi_{sp,i} = \nabla_s \psi_{sp,i}, \quad \nabla_s \varphi_{spt,i} = \nabla_s \psi_{spt,i}. \quad (14)$$

We further represent the renormalized potentials in the form

$$\psi_{sp,i} = \varphi_{s,i} + \varphi_{p,i} + \omega_{sp,i}, \quad (15)$$

$$\psi_{spt,i} = \varphi_{s,i} + \varphi_{p,i} + \varphi_{t,i} + \omega_{sp,i} + \omega_{st,i} + \omega_{pt,i} + \omega_{spt,i}. \quad (16)$$

Expressions (15) and (16) make it possible to construct successive approximations for closure of the original chain of equations. Putting successively

$$\omega_{sp} = \sum_{i \neq s,p}^N \omega_{sp,i} = 0, \quad \omega_{spt} = \sum_{i \neq s,p,t}^N \omega_{spt,i} = 0, \quad (17)$$

$$\omega_{sp} \neq 0, \quad \omega_{spt} = 0 \quad (18)$$

and using the recurrence relations between functions (4)-(6)

$$F(s) = \int_{v_p} F(s, p) d(p), \quad F(s, p) = \int_{v_t} F(s, p, t) d(t), \quad (19)$$

we reach the following systems of closed integral equations for the average force potentials and the functions ω just introduced:

$$\exp(-\beta\varphi_{s,p}) = c_p \int_{v_p} \exp[-\beta(\Phi_{sp} - \varphi_{p,s} + \varphi_p)] d(p), \quad (20)$$

$$\exp(-\beta\varphi_{s,p}) = c_p \int_{v_p} \exp[-\beta(\Phi_{sp} - \varphi_{p,s} + \varphi_p + \omega_{sp})] d(p),$$

$$\exp[-\beta(\omega_{sp,t} - \varphi_{s,t} - \varphi_{p,t})] = c_t \int_{v_t} \exp[-\beta(\Phi_{st} + \Phi_{pt} + \omega_{st} + \omega_{pt} - \omega_{st,p} - \omega_{pt,s} - \varphi_{t,s} - \varphi_{t,p})] d(t). \quad (21)$$

The procedure described can be extended similarly to higher equations of the chain.

It can be shown [11] that in any approximation the configuration integral of the system is determined by the expression

$$Q_N = \prod_{i=1}^N \int_{v_i} \exp(-\beta\varphi_i) d(i). \quad (22)$$

The role of the approximation appears to be that φ_i is the solution of the corresponding system of nonlinear integral equations; in other words, the potential of the total average force is calculated with account of correlations of a given order.

Since no assumptions were made concerning the material structure in obtaining the closed systems of equations, these equations are valid for any phase.

We use now a milder approximation, the system of equations (20) for describing the structural and thermodynamic properties of a molecular crystal with central interactions. We rewrite this equation:

$$\exp(-\beta\varphi_{s,p}) = \int_{v_p} \exp[-\beta(\Phi_{sp} - \varphi_{p,s})] F_p(p) d(p). \quad (23)$$

In the equilibrium state, particle displacements in the crystal from their equilibrium positions, the lattice sites, are small in comparison with the interparticle distances. Consequently, the single-particle function $F(p)$ must have a sharp peak in the site region, and since the right-hand side of (23) contains a multiplier of this function, the main contribution to the integral is provided by the region near the site. Since the statistical scheme under consideration takes into account only single-particle filling of cells, which corresponds to an ideal crystal, the region of integration in (23) must be the Wigner-Seitz cell; this is also assumed in what follows, so that it fully reflects the point symmetry of the crystal.

The presence of functions with sharp peaks under the integral sign justifies the use of the Laplace method for multiple integrals (see [12]) in calculating the right-hand side of (23).

In practice, it is necessary to calculate integrals of the form

$$I(y, \lambda) = \int_{\mathcal{V}} f(y, \mathbf{x}) \exp[\lambda S(\mathbf{x})] d\mathbf{x}, \quad (24)$$

where λ is a large positive number, the function $S(\mathbf{x})$ has a maximum at zero, i.e.,

$$\nabla S(0) = 0, \quad \nabla \nabla S(0) < 0, \quad (25)$$

and function $f(y, \mathbf{x})$ is continuous in both variables in the region under consideration. Under these conditions the following expansion is valid for integral (24)

$$I(y, \lambda) \sim \lambda^{-3/2} \exp[\lambda S(0)] \sum_{k=0}^{\infty} \alpha_k \lambda^{-k}. \quad (26)$$

Direct application of this technique while maintaining the first two terms of the asymptotic expansion to Eq. (21) makes it possible to obtain the following equations for the static part of the average force potential and its first two derivatives at the site (we further consider only cubic lattices):

$$\varphi_{s,p}^{(0)} = \frac{1}{2} \{ \Phi_{sp}^{(0)} - \beta^{-1} \ln [1 - (2\sigma)^{-1} (\Phi_{sp}^{(2)} - \beta g_{sp}^2 - \Delta\varphi_{s,p})] \}, \quad \nabla\varphi_{s,p} = k_{sp} \mathbf{R}_{sp} / R_{sp}, \quad k_{sp} = g_{sp} - \Phi'_{sp}, \quad (27)$$

$$g_{sp} = \frac{2\beta\Phi_{sp}'' - \Phi_{sp}^{(3)}}{2\beta\sigma \{1 - (2\sigma)^{-1} (\Phi_{sp}^{(2)} - \beta g_{sp}^2 - \Delta\varphi_{s,p})\}}, \quad (28)$$

$$\Delta\varphi_{s,p} = \Phi_{sp}^{(2)} + \beta g_{sp}^2 + g_{sp} \frac{\Phi_{sp}^{(4)} - 2\beta(K_{sp} + \Phi_{ps}^{(3)} g_{sp})}{2\beta\Phi_{sp}'' g_{sp} - \Phi_{sp}^{(3)}}. \quad (29)$$

Here

$$\begin{aligned}\Phi_{sp}^{(2)} &= \Phi_{sp}^{II} + 2\Phi_{sp}^I/R_{sp}; \quad \Phi_{sp}^{(3)} = \Phi_{sp}^{III} + (2/R_{sp})[\Phi_{sp}^{II} - \Phi_{sp}^I/R_{sp}]; \\ \Phi_{sp}^{(4)} &= \Phi_{sp}^{IV} + 4\Phi_{sp}^{III}/R_{sp}; \quad K_{sp} = [\Phi_{sp}^{II}]^2 + 2[\Phi_{sp}^I/R_{sp}].\end{aligned}\quad (30)$$

R_{sp} is the distance between sites, and the values of all quantities are taken at the sites. Expressions (27)-(30) imply, in particular, that maintaining two terms of the asymptotic series makes it possible to take into account anharmonicities up to fourth order, inclusive.

Finally, for the quantity σ , which in the combination $\beta\sigma = \lambda$ practically satisfies the role of a large parameter in expansion (26), we have an equation following from definition (7):

$$\sigma = \frac{1}{3} \Delta\varphi_s = \frac{1}{3} \sum_{p \neq s}^N \Delta\varphi_{s,p}. \quad (31)$$

By translational invariance, σ is identical for all particles, and therefore we omit its subscript.

The solution of the system of equations (27)-(29) determines the single and binary distribution functions, which in the approximation under consideration are

$$F(s) = (\beta\sigma/2\pi)^{3/2} \exp\left(-\frac{\beta\sigma}{2} \mathbf{u}_s^2\right), \quad (32)$$

$$F(s, p) = (\beta\sigma/2\pi)^3 \exp\left\{-\beta\left[\Phi_{sp} - \varphi_{s,p} - \varphi_{p,s} + \frac{\sigma}{2}(\mathbf{u}_s^2 + \mathbf{u}_p^2)\right]\right\}, \quad (33)$$

where \mathbf{u}_s is the particle deviation from the lattice site.

Putting these expressions together with the solutions of the system of equations (27)-(29), (31), one can directly calculate thermodynamic quantities, represented in terms of pair interaction potentials, as well as structural factors, e.g., the mean-square particle displacement from the site and the displacement correlator of two particles at different sites:

$$\langle \mathbf{u}_s \mathbf{u}_s \rangle = (\beta\sigma)^{-1} E, \quad (34)$$

$$\langle \mathbf{u}_s \mathbf{u}_p \rangle = \frac{(\Phi_{sp}^{(2)} - \beta g_{sp}^2) \mathbf{e}_{sp} \mathbf{e}_{sp} + (E - 3\mathbf{e}_{sp} \mathbf{e}_{sp}) \Phi_{sp}^I/R_{sp}}{\beta\sigma^4 [1 - (2\sigma)^{-1}(\Phi_{sp}^{(2)} - \beta g_{sp}^2 - \Delta\varphi_{s,p})]}, \quad (35)$$

whence it follows that in a cubic lattice particle displacements in different directions are independent, while the displacements of two particles are correlated in arbitrary directions.

The results of calculating the quantities $\langle \mathbf{u}_s^2 \rangle$ and $\langle \mathbf{u}_s \cdot \mathbf{u}_p \rangle$ are given in Fig. 1a, b. It is seen that the values of the mean-square displacement and of the pair correlator increase with both temperature and molecular volume.

Along with the calculation by means of distribution functions, thermodynamic quantities can also be calculated in terms of the system configuration integral

$$Q_N = [(2\pi/\beta\sigma)^{3/2} \exp(-\beta\varphi^{(0)})]^N, \quad (36)$$

where $\varphi^{(0)} = \sum_{p \neq s}^N \varphi_{s,p}^{(0)}$, and the subscript of $\varphi^{(0)}$ is omitted, as well as σ . The free energy is, consequently,

$$F = Nf = N \left(A\theta - 3\theta \ln \theta + \frac{3}{2} \theta \ln \sigma + \varphi^{(0)} \right), \quad (37)$$

where A is independent of θ and v .

Differentiating the latter expression with respect to the corresponding variables, one obtains all the interesting thermodynamic quantities [13]:

pressure

$$p = -\frac{R}{3v} \left(\frac{\partial f}{\partial R} \right)_\theta, \quad (38)$$

isothermal compressibility

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_\theta = -3/R \left(\frac{\partial p}{\partial R} \right)_\theta, \quad (39)$$

where R is the nearest neighbor distance,

the internal energy

$$\langle U_N \rangle = F - \theta \frac{\partial F}{\partial \theta}, \quad (40)$$

the thermal expansion coefficient

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \kappa_T \left(\frac{\partial p}{\partial T} \right)_v \quad (41)$$

etc.

Figures 2 and 3 show, respectively, results of calculating the pressure and the isothermal compressibility. In the concrete calculations we used the Lennard-Jones potential. Comparison with the experimental pressure data makes it possible to claim satisfactory agreement. The worsening agreement with increasing volume can, obviously, be explained by the increasing role of anharmonicity and by the insufficiency of including two asymptotic terms only in this region. The calculated curve for the isothermal compressibility differs from experiment by a constant quantity. This deviation can be eliminated by changing the parameters of the potential, the accuracy in whose determination is not large. This type of fit, however, was not performed in the present work. Similar results are also available for other quantities [11].

We stress that there is no real difficulty in including further terms of the asymptotic expansion (26), which leads to more complete account of anharmonicity and makes it possible to extend the theory to the region immediately adjacent to the melting curve. This has the further justification that the original integral equation was successfully applied to studying the properties of simple liquids [14], and the exact numerical solution [9] manifests the crystal-liquid phase transition.

NOTATION

$F(s)$, $F(s, p)$, $F(s, p, t)$, one-, two-, and three-particle distribution functions; $\nabla_s \equiv \partial/\partial q_s$, $\beta^{-1} = \theta = kT/\varepsilon$, reduced temperature; k , Boltzmann constant; ε and r , parameters of the Lennard-Jones potential; T , absolute temperature; v , reduced molecular volume; $\phi_{sp} \equiv \phi(|q_s - q_p|)$, interaction potential; c_s , c_{sp} , c_{spt} , normalization factors; φ , ψ , average force potentials; Q_N , configuration integral; F , free energy; and E , unit matrix.

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