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MOLECULAR-STATISTICAL DESCRIPTION OF THE SPECIFIC HEAT OF THERMAL-VACANCY CRYSTALS. 1. STATISTICAL MODEL OF ALLOWANCE FOR THE CONTRIBUTION OF THE VACANCY SUBSYSTEM TO THE LATTICE SPECIFIC HEAT OF CRYSTALS

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A simple statistical model of a condensed system with pair particle interaction, which is described by the Lennard-Jones potential, has been proposed. Under the assumption that the probability of filling a microcell pair is equal to the product of the probabilities of filling single cells, a variational problem on minimization of free energy by the model's internal parameter has been formulated. An analytical expression for the addition to the vibrational specific heat of a molecular vacancy crystal has been obtained. A refined model in which the correlation in filling microcell pairs with pores is allowed for has been considered; a refined expression for the addition to the vibrational specific heat, which contains the corresponding small corrections, has been obtained.

Keywords: *condensed molecular system, thermal vacancies, statistical model, correlation, conditional-distribution method, correlative functions, average-force potential, lattice specific heat.*

Introduction. The classical theory of heat capacity of crystals and the well-known Einstein and Debye models determine the functional dependence of the crystals' specific heat on temperature. In these models, specific heat is entirely determined by kinetic and potential energies in the approximation of classical or quantum oscillators (dependent ones in the Einstein model and those independent in the Debye model). However, these models disregard the presence of defects and primarily thermal vacancies, i.e., free lattice sites whose equilibrium concentration is dependent on the system's thermodynamic parameters, ranging in type in the crystals. This subsystem of point defects in the crystals forms two-dimensional (dislocations) and three-dimensional (e.g., pores) defects under actual conditions. The issue of the specific heat as a function of the molecular crystal volume which, e.g., changes under the conditions of uniform compression, i.e., deformation, has not been dealt with either. The earlier two-level molecular-statistical description of nonuniformly deformed defect molecular crystal lattices [1–4] enables us to considering the issue of the influence of the thermal-vacancy subsystem on the thermophysical properties and primarily heat capacity of defect crystals. This has become possible since the proposed statistical model of uniaxial deformation of crystals allows for the discreteness of material under actual conditions [5], at least on the lowest microscopic level of theoretical description. This model makes it possible to track, with the correlative functions of the Rott conditional-distribution method [6], the microstructural change in a deformable crystal [7], which is produced by the increase in the deformation and determines the entropy production of a solid body. The developed procedure of calculation of the free energy of a deformed solid body [8] allows for the potential deformation energy (force factor) and structural features of a material (entropy factor) using the statistical method of conditional distributions and the variational method of thermodynamic functionals [9].

Statistical Model of a Condensed Molecular Medium. We have formulated earlier, with the two-level molecular-statistical approach [4], a simple statistical model of a condensed system with pair particle (molecular) interaction which is described by the Lennard-Jones potential. In accordance with the conditional-distribution method [6], the entire volume V of the medium is divided into M equal microcells of volume ω ($\omega = V/M$) so that the number of

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these microcells is larger than the number of particles ($M > N$). The microcell volume must be rather small for the probability of two particles entering simultaneously one microcell to be disregarded. In computing the potential part of the internal energy U of a system of N molecules distributed by M microcells, we use the statistical expression [3, 4] for the occupation number n_{ij} of microcell pairs

$$n_{ij} = n + \frac{1 - \sqrt{1 + 4n(1-n)z_{ij}}}{2z_{ij}}, \quad n = \frac{N}{M}, \quad i, j = 1, 2, ..., M. \tag{1}$$

The quantity z_{ij} is the average value of the Mayer function ($\Phi(|\mathbf{r}_i - \mathbf{r}_j|)$ is the Lennard-Jones potential)

$$f_{ij} = \exp\left(-\frac{\Phi(|\mathbf{r}_i - \mathbf{r}_j|)}{kT}\right) - 1, \tag{2}$$

which has been obtained [4] from the averaging of the function f_{ij} over microvolumes ω_i ($\mathbf{r}_i \subset \omega_i$) and ω_j ($\mathbf{r}_j \subset \omega_j$) using the two-particle correlative function $\hat{F}_{11}(\mathbf{r}_i, \mathbf{r}_j)$ of the Rott conditional-distribution method [6]:

$$\hat{F}_{11}(\mathbf{r}_i, \mathbf{r}_j) = C_{ij} \exp\left(-\frac{1}{kT}\Phi(|\mathbf{r}_i - \mathbf{r}_j|)\right) \exp\left(-\frac{1}{kT}\left[\sum_{k \neq i,j}^{M} \varphi_{ik}(\mathbf{r}_i) + \sum_{k \neq i,j}^{M} \varphi_{jk}(\mathbf{r}_j)\right]\right). \tag{3}$$

The function $\hat{F}_{11}(\mathbf{r}_i, \mathbf{r}_j)$ containing the normalization constant C_{ij} and the potentials φ of average forces [1–4] describes the distribution of two particles (molecules), one of which is in the volume ω_i, and the other is in the volume ω_j. In final form, z_{ij} is expressed by the average values $\varphi_{ij}(n, T)$ of the average-force potentials

$$z_{ij} = \langle f_{ij} \rangle = \exp\left(-\frac{\varphi_{ij}(n, T)}{kT}\right) - 1. \tag{4}$$

With the formulas (known from thermodynamics and statistical physics) for the free energy F, the combinatorial part S_0 of the entropy S of fermion gas, and the potential part of the internal energy U, we obtain a rather simple mathematical model of a homogeneous ($n_i = n_j = n$) condensed molecular medium:

$$F = U - TS, \tag{5}$$

$$S \simeq S_0 + \Delta S = -kM[n \ln n + (1-n)\ln(1-n)] + \Delta S, \tag{6}$$

$$U \simeq \frac{1}{2} \sum_{i=1}^{M} \sum_{j \neq i}^{M} n_{ij} \varphi_{ij}. \tag{7}$$

The quantity ΔS allows for the contribution of the binary correlations between the system's molecules (a-sort particles) and vacancies (b-sort quasiparticles), which are statistically distributed by M microcells:

$$\Delta S \simeq -\frac{kM}{2} \sum_{j \neq i}^{M} \sum_{\mu,\nu = a,b} n_{ij}^{\mu\nu} \ln \frac{n_{ij}^{\mu\nu}}{n_i^{\mu} n_j^{\nu}} = -\frac{kM}{2} \sum_{j \neq i}^{M} \left(n_{ij}^{aa} \ln \frac{n_{ij}^{aa}}{n_i^a n_j^a} + 2n_{ij}^{ab} \ln \frac{n_{ij}^{ab}}{n_i^a n_j^b} + n_{ij}^{bb} \ln \frac{n_{ij}^{bb}}{n_i^b n_j^b} \right). \tag{8}$$

It is seen that the addition ΔS to the combinatorial entropy S_0 contains correlators $p_{ij}^{\mu\nu} = n_{ij}^{\mu\nu}/(n_i^{\mu} n_j^{\nu})$ (μ and $\nu = a$ and b) which are expressed by the numbers of occupation of single microcells numbered i or j (n_i^{μ} and n_j^{ν}) by particles and quasiparticles and the occupation numbers of various pairs of cells numbered i or j ($n_{ij}^{\mu\nu}$ and $n_{ij}^{aa} = n_{ij}$).

In the region of the crystalline state, the distribution functions are strongly localized in the vicinity of crystal-lattice sites; therefore, the potential energy U can be expanded into the static energy U_0 of the lattice of vacancies and the energy U_{vibr} related to the vibrational motion of particles in the region of localization of the distribution functions:

$$U = U_0 + U_{\text{vibr}}\,. \tag{9}$$

In the first approximation, which allows for the interaction of each molecule only with the molecules in the 12 nearest microcells of the face-centered lattice (approximation of the nearest neighbors for which $n_{ij}^{aa} = n_{ij}^{(1)}$), we obtain, for the static potential part of the internal energy U_0, the following expression:

$$U_0 \simeq 6Mn_{ij}^{(1)}\varphi_1(R) = \frac{6N\varepsilon}{n\upsilon^2}\left(\frac{\sigma^{12}}{n^2\upsilon^2} - 2\sigma^6\right), \quad \omega = n\upsilon\,, \quad \upsilon = \frac{V}{N}\,, \tag{10}$$

where

$$\varphi_1(R) \simeq \Phi(R) = 4\varepsilon\left(\frac{\sigma^{12}}{R^{12}} - \frac{\sigma^6}{R^6}\right) = \varepsilon\left(\frac{\sigma^{12}}{\omega^4} - \frac{2\sigma^6}{\omega^2}\right) = \frac{\varepsilon}{n^2\upsilon^2}\left(\frac{\sigma^{12}}{n^2\upsilon^2} - 2\sigma^6\right). \tag{11}$$

Here $\Phi(R)$ is the value of the Lennard-Jones potential for two molecules found in two neighboring sites of the crystal lattice ($R = \sqrt[6]{2}\,\omega^{1/3}$ is the parameter of the face-centered lattice) and ε and σ are parameters of the Lennard-Jones potential.

Contribution of the Vacancy Subsystem to the Lattice Specific Heat without Allowance for the Correlation of the Conditional-Distribution Method in Filling Microcell Pairs. Numerical calculations show that in the region of crystalline state (away from the fusion line, where $\upsilon < 1$), by virtue of the low concentration c of vacancies ($c = 1 - n$), the probability of filling a pair of the nearest microcells is $n_{ij} \simeq n^2$. Therefore, we can use, in the zeroeth approximation for the free energy F_0 of a vacancy crystal, the relation in which F_0, U_0, and S_0 are expressed in units of ε, and the volumes υ and ω are expressed in units of σ^3 ($\theta = kT/\varepsilon$ is the reduced temperature):

$$F_0 = U_0 + U_{\text{vibr}} - TS_0 = \frac{\theta V}{\upsilon}\left[\ln n + \left(\frac{1}{n} - 1\right)\ln(1-n)\right] + \frac{6V}{\upsilon^3}\left(\frac{1}{n^3\upsilon^2} - \frac{2}{n}\right) + U_{\text{vibr}}\,. \tag{12}$$

In the existing models of the crystal's specific heat (Einstein and Debye models), the energy U as a function of the concentration of vacancies is totally disregarded; therefore, we assume that the vibrational energy U_{vibr} is weakly dependent on n. Variation by the internal parameter n of the theory yields an equation nonlinear with respect to the equilibrium concentration n, i.e.,

$$\frac{\partial F_0}{\partial n} = -\frac{\theta V}{n^2\upsilon}\ln(1-n) + \frac{6V}{n^2\upsilon^3}\left(2 - \frac{3}{n^2\upsilon^2}\right) = 0 \tag{13}$$

and an expression for the vacancy concentration c:

$$c = \exp(a/\theta)\,, \tag{14}$$

$$a = \frac{6}{\upsilon^2}\left(2 - \frac{3}{n^2\upsilon^2}\right). \tag{15}$$

It is well known that the molecular specific heat of a thermodynamic system at constant volume is determined from the formula

$$C_\upsilon = \left(\frac{\partial u}{\partial \theta}\right)_\upsilon = \left(\frac{\partial u_0}{\partial \theta}\right)_\upsilon + \left(\frac{\partial u_{\text{vibr}}}{\partial \theta}\right)_\upsilon , \tag{16}$$

$$u_0 = \frac{U_0}{N} = \frac{6}{n\upsilon^2}\left(\frac{1}{n^2\upsilon^2} - 2\right). \tag{17}$$

When the value of the volume υ is fixed, the energy is dependent on the concentration n which, being the solution of Eq. (13), is dependent on the temperature θ. Therefore, the addition to the vibrational specific heat is determined by the expression

$$\Delta C_\upsilon = \left(\frac{\partial u_0}{\partial \theta}\right)_\upsilon = \left(\frac{\partial u_0}{\partial n}\right)_{\upsilon,\theta}\left(\frac{dn}{d\theta}\right)_\upsilon . \tag{18}$$

We find the partial derivative $(\partial u_0/\partial n_n)_{\upsilon,\theta}$, differentiating expression (17) for the energy u_0 with respect to n, for a fixed υ value (u_0 is independent of the temperature in the zero approximation). Then we have

$$\left(\frac{\partial u_0}{\partial n}\right)_{\upsilon,\theta} = \frac{6}{n^2\upsilon^2}\left(2 - \frac{3}{n^2\upsilon^2}\right) = \frac{a}{n^2} . \tag{19}$$

To determine the derivative $(\partial n/\partial\theta)_\upsilon$ we implicitly differentiate Eq. (13) with respect to the temperature θ. As a result we obtain

$$\left(\frac{\partial^2 F_0}{\partial n \partial \theta}\right)_\upsilon + \left(\frac{\partial^2 F_0}{\partial n^2}\right)_{\upsilon,\theta}\left(\frac{dn}{d\theta}\right)_\upsilon = 0 \tag{20}$$

or

$$-\frac{1}{1-n}\left(\frac{dn}{d\theta}\right)_\upsilon = -\frac{6}{\theta^2\upsilon^2}\left(2 - \frac{3}{n^2\upsilon^2}\right) + \frac{36}{\theta n^3\upsilon^4}\left(\frac{dn}{d\theta}\right)_\upsilon .$$

From the last equation, we express the derivative $(\partial n/\partial\theta)_\upsilon$:

$$\left(\frac{dn}{d\theta}\right)_\upsilon = -\frac{\left(\frac{\partial^2 F_0}{\partial n \partial \theta}\right)_\upsilon}{\left(\frac{\partial^2 F_0}{\partial n^2}\right)_{\upsilon,\theta}} = \frac{\frac{6}{\theta^2\upsilon^2}\left(2 - \frac{3}{n^2\upsilon^2}\right)}{\frac{1}{c} + \frac{36}{\theta n^3\upsilon^4}} = \frac{1}{\theta^2\left(\exp\left(-\frac{a}{\theta}\right) + \frac{b}{\theta}\right)} , \tag{21}$$

$$b = \frac{36}{n^3\upsilon^4} > 0 . \tag{22}$$

Substituting expressions (19) and (21) into formula (18), we finally write

$$\Delta C_\upsilon = \frac{a^2}{\theta^2 n^2\left[\exp\left(-\frac{a}{\theta}\right) + \frac{b}{\theta}\right]} \tag{23}$$

for the addition to the crystals' vibrational specific heat.

Let us analyze formula (23) in the low-temperature region, passing to the limit $\theta \to 0$ (strongly cooled crystal). It is seen from formulas (14) and (15) that when the volume $\upsilon < 1$ is fixed and the temperature tends to zero the concentration c tends to zero, too ($n = 1 - c \to 1$). Therefore, as the absolute zero is approached, we can disregard the term b/θ in the denominator of expression (23) compared to the exponent, since we have $a < 0$ for $\upsilon \le 1$. Then, in the low-temperature approximation in question, we obtain

$$\Delta C_\upsilon \simeq \frac{a^2}{\theta^2 n^2} \exp\left(\frac{a}{\theta}\right) = \frac{a^2 c}{\theta^2 n^2} . \tag{24}$$

It follows from expression (24) that in the developed classical statistical model of a condensed medium, the addition to the lattice's vibrational specific heat tends to zero in an exponential manner with decrease in the temperature ($\theta \to 0$). The vibrational lattice specific heat in the Einstein model varies in the same manner. Conceivably the analogy will be revealed when $\theta \to 0$ might be a consequence of the fact that quantum oscillators are assumed to be independent in the Einstein model, whereas in the (zeroeth) classical approximation under study, the correlation on filling pairs of neighboring microcells with molecules is disregarded ($n_{ij} \simeq n^2$).

It is of interest to compare the parameters of the obtained formula (24) and the Einstein expression for the vibrational specific heat C_υ^* per crystal molecule:

$$C_\upsilon^* = \frac{C_\upsilon^{\mathrm{E}}}{N_{\mathrm{A}}} = 3k\left(\frac{h\nu}{kT}\right)^2 \exp\left(-\frac{h\nu}{kT}\right). \tag{25}$$

Comparing expression (24) and (25), we see that a certain frequency ν^* determined by the expression

$$\frac{h\nu^*}{kT} = -\frac{a}{\theta} \Rightarrow \nu^* = -\frac{kTa}{h\theta} = -\frac{\varepsilon a}{h} \tag{26}$$

can be placed in correspondence with the oscillator frequency ν used in the Einstein model. It follows from expression (26) that the parameter ν^* is a function of the thermodynamic parameters of state of a defect crystal, i.e., ν^* is dependent on the molecular volume υ and the concentration n which, in the thermodynamic-equilibrium state, is a function of the temperature θ and the volume υ. Numerical evaluation has shown that the parameter ν^* is approximately equal to 10^{13}–10^{14} Hz.

Allowance for the Correlation in Calculating the Specific Heat of a Crystal Lattice with Thermal Vacancies. Using the determination of the molecular specific heat (16), we write an expression for the addition to the crystal's vibrational specific heat in a form analogous to (18):

$$\Delta C_{1\upsilon} = \left(\frac{\partial u_1}{\partial n}\right)_{\upsilon,\theta} \left(\frac{dn}{d\theta}\right)_\upsilon . \tag{27}$$

Here $u_1 = U_1/N$ is the static part of the correlated-lattice energy per molecule in the first approximation corresponding to allowance for the correlation in filling pairs of neighboring microcells of ω_i and ω_j.

In computing the energy U_1 and the entropy S_1 of the model, we use the expression obtained earlier [4] for the occupation numbers n_{ij} of pairs of neighboring microcells of volume ω_i and ω_j:

$$n_{ij} \simeq n + \frac{1 - \sqrt{1 + 4n(1-n)z}}{2z} , \tag{28}$$

where the quantity z in the approximation of interaction with 12 nearest neighbors is expressed by $\varphi_1(R)$ (formula (11)) with dimensionless quantities

$$z = \exp\left\{-\frac{\Phi(R)}{kT}\right\} - 1 = \exp\left\{-\frac{1}{\theta n^2 \upsilon^2}\left(\frac{1}{n^2 \upsilon^2} - 2\right)\right\} - 1 . \tag{29}$$

The concentration c of vacancies in the region of crystalline state is low ($c < 10^{-3}$ away from the fusion line). Therefore, expanding (28) in the small parameter x ($x = 4ncz$), we obtain, for the occupation numbers n_{ij} of a pair of the nearest cells, the expression

$$n_{ij} \simeq n^2 + n^2 c^2 z = n^2 (1 + \xi_1) . \tag{30}$$

where

$$\xi_1 = c^2 z << 1 . \tag{31}$$

Then the static potential part of the internal energy of the correlated model, with account for formula (30), will be determined as

$$U_1 = \frac{n_{ij} U_0}{n^2} = U_0 + U_0 c^2 z = U_0 (1 + \xi_1) . \tag{32}$$

Allowance for the correlation in filling pairs of neighboring microcells with particles gives rise to the addition ΔS to the combinational part of the entropy S_0 (expression (6)):

$$S_1 = S_0 + \Delta S = S_0 + M \Delta S^* , \tag{33}$$

where

$$\Delta S^* \simeq -\frac{k}{2} \sum_{j \neq i}^{M} \sum_{\mu,\nu = a,b} n_{ij}^{\mu\nu} \ln \frac{n_{ij}^{\mu\nu}}{n_i^{\mu} n_j^{\nu}} = -6k\left(n_{aa} \ln \frac{n_{aa}}{n_a n_a} + 2 n_{ab} \ln \frac{n_{ab}}{n_a n_b} + n_{bb} \ln \frac{n_{bb}}{n_b n_b}\right). \tag{34}$$

Here ΔS^* is the addition to the system's entropy S_0 per microcell; n_{aa}, n_{ab}, and n_{bb} are the occupation numbers that determine the corresponding probabilities of filling simultaneously a pair of neighboring microcells with molecules (a-sort particles, $n_a = n$) and with noninteracting quasiparticles whose concentration is equal to the concentration of vacancies (b-sort particles, $n_b = c$).

The normalization conditions for the numbers of occupation of microcell pairs by particles (μ and $\nu = a$) and quasiparticles (μ and $\nu = b$)

$$n_{aa} + n_{ab} = n_a , \quad n_{bb} + n_{ba} = n_b \tag{35}$$

and expression (30) make it possible to establish a relationship between the occupation numbers $n_{\mu\nu}$ of microcell pairs and the concentration of particles and vacancies:

$$n_{aa} = n_{ij} \simeq n^2 (1 + c^2 z) , \quad n_{ab} = n_{ba} = n - n_{ij} \simeq nc (1 - ncz) , \quad n_{bb} = c - n_{ab} \simeq c^2 (1 + n^2 z) . \tag{36}$$

Expanding the logarithms in formula (34) in a small parameter, which is the vacancy concentration c, we obtain the expression for the entropy S_1 of the first approximation with allowance for binary correlations

$$S_1 \simeq -kN\left[\ln n + \frac{c}{n} \ln c + 6nc^2 z^2\right] = S_0 + \xi_2 , \tag{37}$$

where

$$\xi_2 = -\,6kNnc^2z^2 \,. \tag{38}$$

The expression for the free energy F_1 of the model, with account for formulas (32) and (37), will be transformed to the following form:

$$F_1 = U_1 - TS_1 = U_0 + U_0\xi_1 - TS_0 - T\xi_2 = F_0 + \xi_3 \,, \tag{39}$$

where

$$\xi_3 = U_0\xi_1 - T\xi_2 = Nc^2z\left[\frac{6}{n\upsilon^2}\left(\frac{1}{n^2\upsilon^2} - 2\right) + 6\theta nz\right]. \tag{40}$$

Variation of expression (39) by the model's internal parameter n yields the equation (nonlinear with respect to n)

$$\left(\frac{\partial F_1}{\partial n}\right)_{\upsilon,\theta} = \left(\frac{\partial F_0}{\partial n}\right)_{\upsilon,\theta} + \left(\frac{\partial \xi_3}{\partial n}\right)_{\upsilon,\theta} = 0 \,, \tag{41}$$

where

$$\left(\frac{\partial \xi_3}{\partial n}\right)_{\upsilon,\theta} = \frac{6N}{n\upsilon^2}\left[\frac{1}{n}\left(2 - \frac{3}{n^2\upsilon^2}\right)c^2z + \left(\frac{1}{n^2\upsilon^2} - 2\right)\left(-\,2cz + c^2\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta}\right)\right]$$

$$+\,6\theta N\left[(1 - 4n + 3n^2)\,z^2 + 2nc^2z\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta}\right], \tag{42}$$

$$\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta} = -\frac{1}{\theta}\left(\frac{\partial \varphi_1}{\partial n}\right)_{\upsilon}(z + 1)\,, \tag{43}$$

$$\left(\frac{\partial \varphi_1}{\partial n}\right)_{\upsilon} = \frac{4}{n^3\upsilon^2}\left(1 - \frac{1}{n^2\upsilon^2}\right). \tag{44}$$

Using the expression for the static energy u_1 per molecule

$$u_1 = U_1/N = u_0 + u_0\xi_1 \,, \tag{45}$$

we find the partial derivative $(\partial u_1/\partial n)_{\upsilon,\theta}$ which is involved in expression (27) for the addition $\Delta C_{1\upsilon}$ to the vibrational molecular specific heat

$$\left(\frac{\partial u_1}{\partial n}\right)_{\upsilon,\theta} = \left(\frac{\partial u_0}{\partial n}\right)_{\upsilon,\theta} + \xi_4 \,, \tag{46}$$

where

$$\xi_4 = \left(\frac{\partial\,(u_0\xi_1)}{\partial n}\right)_{\upsilon,\theta} = \frac{6}{n\upsilon^2}\left[\frac{1}{n}\left(2 - \frac{3}{n^2\upsilon^2}\right)c^2z + c\left(\frac{1}{n^2\upsilon^2} - 2\right)\left(c\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta} - 2z\right)\right]. \tag{47}$$

Implicit differentiation of the variational equation (41) yields

$$\left(\frac{dn}{d\theta}\right)_{\upsilon} = -\left(\left(\frac{\partial^2 F_0}{\partial n \partial\theta}\right)_{\upsilon} + \xi_5\right) \Big/ \left(\left(\frac{\partial^2 F_0}{\partial n^2}\right)_{\upsilon,\theta} + \xi_6\right), \tag{48}$$

where

$$\xi_5 = \left(\frac{\partial^2 \xi_3}{\partial n \partial\theta}\right)_{\upsilon} = \frac{6N}{n\upsilon^2}\left[\frac{1}{n}\left(2 - \frac{3}{n^2\upsilon^2}\right) c^2 \left(\frac{\partial z}{\partial\theta}\right)_{n,\upsilon} + \left(\frac{1}{n^2\upsilon^2} - 2\right)\left(-2c\left(\frac{\partial z}{\partial\theta}\right)_{n,\upsilon} + c^2\left(\frac{\partial^2 z}{\partial n\partial\theta}\right)_{\upsilon}\right)\right]$$

$$+ 6N\left[(1 - 4n + 3n^2)\, z^2 + 2nc^2 z\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta} + \theta\left(2\,(1 - 4n + 3n^2)\, z\left(\frac{\partial z}{\partial\theta}\right)_{n,\upsilon}\right.\right.$$

$$\left.\left. + 2nc^2\left(\left(\frac{\partial z}{\partial\theta}\right)_{n,\upsilon}\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta} + z\left(\frac{\partial^2 z}{\partial n\partial\theta}\right)_{\upsilon}\right)\right)\right], \tag{49}$$

$$\xi_6 = \left(\frac{\partial^2 \xi_3}{\partial n^2}\right)_{\upsilon,\theta} = \frac{6N}{\upsilon^2}\left[\frac{4}{n^3}\left(\frac{3}{n^2\upsilon^2} - 1\right)c^2 z + \left(2 - \frac{3}{n^2\upsilon^2}\right)\frac{c}{n^2}\left(2c\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta} - 4z\right)\right.$$

$$\left. + \frac{1}{n}\left(\frac{1}{n^2\upsilon^2} - 2\right)\left(-4c\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta} + c^2\left(\frac{\partial^2 z}{\partial n^2}\right)_{\upsilon,\theta} + 2z\right)\right]$$

$$+ 6\theta N\left[2\,(3n - 2)\, z^2 + 2nc^2\left(\left(\frac{\partial z}{\partial n}\right)^2_{\upsilon,\theta} + z\left(\frac{\partial^2 z}{\partial n^2}\right)_{\upsilon,\theta}\right) + 4z\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta}(1 - 4n + 3n^2)\right], \tag{50}$$

$$\left(\frac{\partial z}{\partial\theta}\right)_{n,\upsilon} = \frac{1}{\theta^2}\,(z + 1)\,\varphi_1\,, \tag{51}$$

$$\left(\frac{\partial^2 z}{\partial n\partial\theta}\right)_{\upsilon} = \frac{1}{\theta}\left(\frac{\partial\varphi_1}{\partial n}\right)_{\upsilon}\left[\frac{1}{\theta}\,(z + 1) - \left(\frac{\partial z}{\partial\theta}\right)_{n,\upsilon}\right], \tag{52}$$

$$\left(\frac{\partial^2 z}{\partial n^2}\right)_{\upsilon,\theta} = -\frac{1}{\theta}\left(\frac{\partial^2\varphi_1}{\partial n^2}\right)_{\upsilon}(z + 1) - \frac{1}{\theta}\left(\frac{\partial\varphi_1}{\partial n}\right)_{\upsilon}\left(\frac{\partial z}{\partial n}\right)_{\upsilon,\theta}, \tag{53}$$

$$\left(\frac{\partial^2\varphi_1}{\partial n^2}\right)_{\upsilon} = \frac{4}{n^4\upsilon^2}\left(\frac{5}{n^2\upsilon^2} - 3\right). \tag{54}$$

Substituting expressions (46) and (48) into the right-hand side of relation (27), we write the final expression for the addition $\Delta C_{1\upsilon}$ determined by the binary correlations in the particle and vacancy distribution in the space network of M microcells:

$$\Delta C_{1\upsilon} = \left(\left(\frac{\partial u_0}{\partial n} \right)_{\upsilon,\theta} + \xi_4 \right) \left(\frac{\partial n}{\partial \theta} \right)_{\upsilon} = - \frac{\left(\left(\frac{\partial u_0}{\partial n} \right)_{\upsilon,\theta} + \xi_4 \right) \left(\left(\frac{\partial^2 F_0}{\partial n \partial \theta} \right)_{\upsilon} + \xi_5 \right)}{\left(\left(\frac{\partial^2 F_0}{\partial n^2} \right)_{\upsilon,\theta} + \xi_6 \right)} . \qquad (55)$$

Conclusions. Comparing expression (55) to (18) and (21), we see that allowance for the binary correlations in filling various microcell pairs with particles gives rise to small corrections in expression (55) determining the addition to the vibrational lattice specific heat C_υ of a molecular vacancy crystal. The performed analytical investigations create prerequisites for computer-aided numerical calculations.

NOTATION

C_υ, molecular specific heat of the thermodynamic system at constant volume; C_υ^{E}, vibrational specific heat in the Einstein model; $c = 1 - n$, concentration of vacancies; F, free energy of the crystal; F_{11}, conditional correlative distribution functions of molecules near the sites of the lattice formed by microcells; f_{ij}, Mayer function; h, Planck's constant; k, Boltzmann constant; M, number of microcells into which the entire volume V of the system is conceivably subdivided; N, number of the system's particles; N_{A}, Avogadro number; n, occupation numbers of single microcells which are equal to the concentration of particles on the volumetric network of M microcells of a uniformly deformed crystal; n_{ij}, occupation numbers of a microcell pair, which are equal to the probability that each ω_i or ω_j microcell contains one molecule; n_i^{μ} or n_j^{ν}, numbers of occupation of i- or j-numbered microcells by particles of sort μ or ν; $n_{ij}^{\mu\nu}$, occupation numbers of various pairs of i- or j-numbered microcells, i.e., the probability of filling a pair of microcells of ω_i and ω_j with μ and ν particles respectively; $\mathbf{r}$, radius vector of a point in the microcell; S, system's entropy; S_0, combinatorial part of the entropy of the system of N particles on the network of M microcells, which is coincident, in the first F_{11}-approximation of the conditional-distribution method, with the entropy of a fermion gas; T, absolute temperature; U, potential part of the internal energy of the condensed molecular system; U_0, static energy of the crystal lattice with vacancies; V_{vibr}, part of the crystal energy due to the vibrational motion of particles near the lattice sites; $u = U/N$, system's internal energy per molecule; V, system's volume; z, average value of the Mayer function; ΔC_υ, addition to the vibrational lattice specific heat of the crystal; ΔS, addition to the combinatorial entropy, which allows for the contribution of binary correlations in filling various microcell pairs with particles; ε, depth of the potential well corresponding to the Lennard-Jones potential; $\theta = kT/\varepsilon$, reduced temperature, i.e., energy expressed in the units of ε; ν, frequency in the Einstein model; ξ_l (l = 1, 2, 3, 4, 5, and 6), small corrections in the expressions allowing for the correlation of particles in statistical calculation of the specific heat of a molecular vacancy crystal; σ, linear parameter of the Lennard-Jones potential; υ, molecular volume; Φ, pair intermolecular Lennard-Jones potential; φ_{ik} and φ_{jk}, potentials of the average forces of interaction of the molecule in the i- or j-numbered microcell with another molecule distributed in the volume of the k-numbered microcell; φ_1, average-force potential in the approximation of interaction of only the nearest neighbors; ω, microcell volume. Subscripts and superscripts: 0, zeroeth approximation (without allowance for the correlation of the conditional-distribution method in filling microcell pairs); a, microcell occupied by a molecule; b, microcell occupied by a quasiparticle, i.e., a vacant cell; i, j, and k, microcell numbers; μ and ν, sort of particles (μ and $\nu = a$, for molecules; μ and $\nu = b$, for quasiparticles, i.e., vacancies); aa, two microcells numbered i and j, with one molecule in each; ab, i-numbered microcell is filled with one molecule, whereas the j-numbered microcell is empty (vacant), i.e., is filled with a quasiparticle; bb, two i- and j-numbered microcells occupied by quasiparticles, i.e., vacant microcells; ij, cell pairs; 11, first statistical approximation of the Rott conditional-distribution method in which each microcell is occupied by no more than one particle; ^ , normalization per unit; *, auxiliary character.

REFERENCES

1. I. I. Narkevich, A statistical study of the defect crystal lattice relaxation, *Physica A*, **150**, 659–671 (1988).

2. I. I. Narkevich, Statistical study of crystal lattice relaxation in the vicinity of different-nature defects, *Vestsi Akad. Navuk BSSR*, *Ser. Fiz.-Mat. Navuk*, No. 4, 86–92 (1988).
3. I. I. Narkevich, Method of Lagrange multipliers in the problem of normalization of the correlative functions of multicomponent crystals with defects, *Vysokochist. Veshchestva*, No. 1, 67–75 (1990).
4. I. I. Narkevich, *Molecular-Statistical Theory of Inhomogeneous Condensed Media*, Author's Abstract of Doctoral Dissertation (in Physics and Mathematics), St. Petersburg (1993).
5. I. I. Narkevich and A. V. Zharkevich, Molecular-statistical description of nonuniformly deformed specimens. 1. Formulation of the problem and method for solving it, *Inzh.-Fiz. Zh.*, **73**, No. 6, 1313–1319 (2000).
6. I. I. Narkevich, S. I. Lobko, A. V. Zharkevich, and P. P. Kazakov, Molecular-statistical description of nonuniformly deformed specimens. 2. Calculation of the distribution functions of molecules and vacancies in a one-dimensional uniformly deformed statistical extension–compression model. *Inzh.-Fiz. Zh.*, **75**, No. 4, 170–176 (2002).
7. A. V. Zharkevich, Molecular-statistical description of nonuniformly deformed specimens. 3. Calculation of the diagram of extension and compression of a one-dimensional statistical model of deformation of a molecular crystal, *Inzh.-Fiz. Zh.*, **77**, No. 4, 144–149 (2004).
8. L. A. Rott, *Statistical Theory of Molecular Systems* [Russian translation], Nauka, Moscow (1979).
9. F. F. Abraham, On the thermodynamics, structure and phase stability of the nonuniform fluid state, *Phys. Rep.*, **53**, No. 2, 93–156 (1979).