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Binary distribution functions of atoms of simple crystals

A. I. Karasevskii* and V. V. Lubashenko†
Institute for Metal Physics, 36 Vernadsky str., Kiev, 03142, Ukraine

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We propose a method of statistical description of simple crystals and calculation of their thermodynamic functions and equation of state. The method is based on the derivation of an exact expression for the binary distribution function of atomic displacements and a variational procedure for the determination of an effective constant of the quasielastic bond of atoms of the crystal. For rare gas crystals with Morse and Lennard-Jones potentials, we obtained the equation of state and thermodynamic parameters of the solid-state, which are in agreement with experimental data. We also found that a solid-state instability occurs near the observed melting temperature of the crystal, corresponding to a point above which there is no more an equilibrium effective parameter of the quasielastic bond.

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I. INTRODUCTION

The statistical theory of perfect solids was extensively developed in the framework of numerous approaches, which, usually, fall into two classes. Some models are based on the single-particle representation of the crystalline state, concentrating on motion of an individual atom in a self-consistent potential due to interaction with its neighborhood.[1–4] The other, more commonly used, class of models is focused on the collective aspect of the lattice dynamics, representing a solid state by means of a set of normal phonon modes. For example, the formalism of the self-consistent phonon (SCP) theory[5–9] is well known as a good tool for treatment of the dynamics of anharmonic solids. In the first order of this model, the self-consistent harmonic (SCH) approximation,[7,10] the true Hamiltonian of the crystal is approximated by an effective harmonic Hamiltonian with the force constants determined by ensemble averaging the second derivatives of the interatomic potential. This yields a set of self-consistent equations for the phonon frequencies and vibrational amplitudes to be solved iteratively. The SCP theory and its modifications were used successfully to evaluate the dynamical properties of both three-dimensional (3D) crystals[11–15] and plane adsorbed monolayers of atoms.[16–18] Particularly, the improved self-consistent (ISC) model, which is the SCH approximation corrected for cubic anharmonicity, provides a satisfactory description of the phonon spectrum[13,19] and thermodynamic properties of the rare gas (RGC's)[11–13,20,21] crystals, except for temperatures near the melting point, where the iteration process shows poor convergence. This shortcoming is avoided within the effective potential theory,[22–24] developed during the past decade. This powerful technique, based on evaluation of the partition function via the path integral method, was successfully applied to consideration of thermal and elastic properties of crystalline neon.[21] Though both single-particle and collective approaches to the description of the solid state use different approximations as starting points, they give rise to similar results, so that they are rather complementary than contradictory, and the choice of the concrete approach is a question of practical purposes.

The present paper is devoted to a formulation of a statistical model of the equilibrium state of solids, based on a derivation of an exact expression for the binary distribution function of atomic displacements. In this approach, a crystal is represented as a statistical ensemble of regularly located particles with pair interactions, each particle being characterized by its thermal and quantum broadening near the lattice site and by its correlations with the motion of other particles. For such a system, knowledge of the binary distribution function of atomic displacements is fundamental in determining the average potential energy of the interatomic interaction. The method developed in this work allows one to construct binary functions of atoms of simple quasiharmonic crystals at any temperature and pressure. In Sec. II we derive a correlated distribution function of atoms of the whole crystal and propose a method of reducing it to the binary function. This procedure was used to determine the parameters of the binary distribution functions of crystals in one, two, and three dimensions. In Sec. III we evaluate the free energy of a simple crystal with pairwise interaction of atoms in terms of the binary distribution functions, taking into account a contribution due to the cubic anharmonicity of atomic vibrations. Both the free energy and coefficients of the distribution function are parametrized by an effective constant of the quasielastic bond, whose equilibrium value is evaluated by the variational procedure. In Sec. IV we determine the equation of state and other thermodynamic parameters of the RGC's in the framework of the approach developed in Secs. II and III, using the Morse and Lennard-Jones potentials for the representation of interatomic interactions. For the limiting cases of low and high temperatures, we present the analytical expressions for the parameters of the distribution function and thermodynamic characteristics of the crystal. An analysis of the results obtained and their comparison with the experimental data and other theoretical models are given in Sec. IV.

II. DISTRIBUTION FUNCTIONS OF ATOMIC DISPLACEMENTS IN SIMPLE CRYSTALS

In this section we demonstrate a method of explicit calculation of the *N*-particle distribution function of atomic displacements in simple harmonic crystals and its reduction to

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the two-particle function. To illustrate the method, we will consider one-dimensional crystals, two-dimensional triangular crystals and three-dimensional crystals with fcc and bcc lattices as examples.

A. *N*-particle distribution function

We consider a simple perfect crystal containing N atoms of mass M. Let us denote $f_n(\mathbf{q}_1,\mathbf{q}_2,\dots,\mathbf{q}_n)$ as the normalized n-particle distribution function of displacements $\mathbf{q}_1,\mathbf{q}_2,\dots,\mathbf{q}_n$ of atoms $1,2,\dots,n$ from their sites. Due to the collective character of the motion of atoms, the function f_n should incorporate correlations between displacements of atoms. In the harmonic approximation, the collective atomic motion in a crystal is described by a set of normal phonon modes. A normal coordinate corresponding to wave vector $\mathbf{k}$ and branch j is

$$a_j(\mathbf{k})=\left(\frac{M}{N}\right)^{1/2}\sum_{n,\beta} q_{n\beta}e_{j\beta}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{R}_n}, \tag{1}$$

where $q_{n\beta}$ is the βth Cartesian coordinate of the displacement of atom n from its equilibrium position $\mathbf{R}_n$, and $e_{j\beta}(\mathbf{k})$ is the phonon polarization vector in the β direction. Let $X_j(\mathbf{k})$ and $Y_j(\mathbf{k})$ be the real and imaginary parts of the normal coordinate $a_j(\mathbf{k})$, respectively. Because each normal mode is considered as an independent harmonic oscillator, the distribution function of atoms of the crystal can be represented, up to a constant factor, as a product of probability densities $P(X_j(\mathbf{k}))$ and $P(Y_j(\mathbf{k}))$ of the real normal coordinates,

$$f_N\sim\prod_{\mathbf{k},j} P(X_j(\mathbf{k}))P(Y_j(\mathbf{k})),$$

where the wave vector $\mathbf{k}$ runs over a half of the Brillouin zone. The details of the derivation of expressions for $P(X_j(\mathbf{k}))$ and $P(Y_j(\mathbf{k}))$ are given in Appendix A. As a result, the normalized N-particle distribution function is given by

$$f_N=C_N\exp\left[-\sum_{nn'\beta\beta'} B_{nn'}^{\beta\beta'}q_{n\beta}q_{n'\beta'}\right], \tag{2}$$

where C_N is a normalization factor and

$$B_{nn'}^{\beta\beta'}=\frac{M}{N\hbar}\sum_{\mathbf{k},j}\omega_j(\mathbf{k})\tanh\left(\frac{\hbar\omega_j(\mathbf{k})}{2T}\right)\times e_{j\beta}(\mathbf{k})e_{j\beta'}(\mathbf{k})\cos[\mathbf{k}(\mathbf{R}_n-\mathbf{R}_{n'})].$$

Here summation over $\mathbf{k}$ is taken over all the Brillouin zone. The frequency $\omega_j(\mathbf{k})$ of the phonon with wave vector $\mathbf{k}$ and branch j is

$$\omega_j(\mathbf{k})=\sum_{\alpha,\beta} e_{j\alpha}(\mathbf{k})D_{\alpha\beta}(\mathbf{k})e_{j\beta}(\mathbf{k}),$$

where

$$D_{\alpha\beta}(\mathbf{k})=\frac{1}{M}\sum_n{}'(e^{-i\mathbf{k}\cdot\mathbf{R}_n}-1)\Phi_{\alpha\beta}(0n)$$

is the dynamical matrix with $\Phi_{\alpha\beta}(0n)$ being the force constant between atoms 0 and n. If atom n belongs to the sth coordination sphere of atom 0,

$$\Phi_{\alpha\beta}(0n)=-\beta_s\frac{R_{n\alpha}R_{n\beta}}{R_s^2},$$

where $R_s=|\mathbf{R}_n-\mathbf{R}_0|$ is the radius of the sth coordination sphere and β_s is the constant of the quasielastic bond of atoms separated by distance R_s.

Expressions for the distribution function f_N and its coefficients are applicable to any type of simple harmonic crystal and may be extended to the case of a lattice containing more than one atom in an elementary cell.

The matrix $B_{nn'}^{\beta\beta'}$ should possess the symmetry of the crystal lattice. If the lattice is symmetrical with respect to rotation around a k-fold axis, with $k>2$, it is easy to demonstrate that $B_{nn}^{\beta\beta'}=\gamma\delta_{\beta\beta'}$, where

$$\gamma=\frac{M}{N\hbar}\sum_{\mathbf{k},j}\omega_j(\mathbf{k})\tanh\left(\frac{\hbar\omega_j(\mathbf{k})}{2T}\right)e_{j\beta}^2(\mathbf{k}) \tag{3}$$

is independent of n and β. Next, the elements $B_{nn'}^{\beta\beta'}$ with $n\neq n'$ have the most simple form if the coordinate system is chosen so that the x axis passes through sites n and n'. In this case $B_{nn'}^{\beta\beta'}=-\gamma\zeta_s^\beta\delta_{\beta\beta'}$, where the dimensionless positive coefficients $\zeta_s^\beta<1$ describe correlations between displacements of atoms belonging to the sth coordination sphere. Numerical estimation of the coefficients ζ_s^β for crystals with different dimensionality and lattice geometry shows that only the parameter ζ_1^x, describing longitudinal correlations of neighboring atoms, contributes substantially to the distribution function f_N. It is reasonable to retain only the parameter $\zeta_1^x\equiv\zeta$ in the expression for f_N, so that the N-particle distribution function is expressed as

$$f_N=C_N\exp\left[-\gamma\sum_n\left(q_n^2-\zeta\sum_{n'}q_n^xq_{n'}^x\right)\right], \tag{4}$$

where the subscript n' runs over all atoms of the first coordination sphere of atom n, and q_n^x and $q_{n'}^x$ are longitudinal displacements of atoms n and n'—i.e., projections of vectors $\mathbf{q}_n$ and $\mathbf{q}_{n'}$ on the x axis passing through their sites. The coefficient of the longitudinal correlation of two neighboring atoms 0 and n is expressed as

$$\zeta=-\frac{M}{N\hbar\gamma}\sum_{\mathbf{k},j}\omega_j(\mathbf{k})\tanh\left(\frac{\hbar\omega_j(\mathbf{k})}{2T}\right)e_{jx}^2(\mathbf{k})\cos(\mathbf{k}\cdot\mathbf{R}_n). \tag{5}$$

Hereafter $e_{jx}(\mathbf{k})$ denotes the projection of the phonon polarization vector $e_{j\beta}(\mathbf{k})$ on the axis passing through two neighboring sites.

B. Two-particle distribution function

To calculate the average potential energy of the pairwise interatomic interaction, we need a two-particle distribution function $f_2(\mathbf{q}_n,\mathbf{q}_{n'})$, which can be readily derived from the N-particle function f_N in the form (4).

1. One-dimensional crystal

The procedure of the reduction of the N-particle function f_N to the binary distribution function of neighboring atoms is very simple and elucidative in the case of a one-dimensional crystal. First, let us consider a cluster containing atom n and its neighbors $n-1$ and $n+1$. A normalized distribution function of such a cell may be generally represented as

$$\begin{aligned} f_3(q_{n-1},q_n,q_{n+1}) &= \int f_N dq_1\cdots dq_{n-2}dq_{n+2}\cdots dq_N \\ &= C_3\exp\{-\gamma[q_n^2+g(\zeta)(q_{n-1}^2+q_{n+1}^2) \\ &\quad -2\zeta q_n(q_{n-1}+q_{n+1})]\}, \end{aligned} \tag{6}$$

where function $g(\zeta)$ is to be determined. Integrating Eq. (6) over q_{n-1}, we arrive at an expression for $f_2(q_n,q_{n+1})$, which has to be symmetric with respect to q_n and q_{n+1}. This condition leads to a quadratic equation for g with the physical solution

$$g(\zeta)=\frac{1}{2}(1+\sqrt{1-4\zeta^2}).$$

As a result, the distribution function for the atoms n and $n+1$ is given by

$$f_2=C_2\exp\{-\gamma[g(\zeta)(q_n^2+q_{n+1}^2)-2\zeta q_n q_{n+1}]\}. \tag{7}$$

It is evident from Eq. (7) that taking interatomic correlations into account in the two-particle function $f_2(q_n,q_{n+1})$ results in an additional correlative broadening ($g<1$) of the range of localization of atoms n and $n+1$.

2. Two- and three-dimensional crystals

To derive the distribution function of a pair of neighboring atoms in a two- or three-dimensional crystal, let us follow the same procedure as described above. Consider a cell containing an atom (say, atom 0) and its nearest neighbors $1,2,\ldots,z$ (z is the coordination number). The distribution function $f_{z+1}(\mathbf{q}_0,\mathbf{q}_1,\ldots,\mathbf{q}_z)$ of atoms of such a cell may be obtained from f_N by integration of Eq. (4) over coordinates of all atoms of the crystal except $z+1$ atoms of the cell. In general, it should appear as

$$f_{z+1}=C_{z+1}\exp\left\{-\gamma\left[q_0^2+\sum_{n=1}^{z}[\tilde{g}(\zeta)q_n^2-2\zeta q_0^x q_n^x]\right]\right\}, \tag{8}$$

TABLE I. Coefficients of the two-particle distribution functions and zero- and high-temperature correlation parameters for different types of lattice geometry.

Lattice	$g_l(\zeta)$	$\chi(\zeta)$	ζ_0	$\zeta_{\rm H}$
1D	$\frac{1}{2}(1+\sqrt{1-4\zeta^2})$	1	1/3	1/2
2D	$1-2\zeta^2+\frac{\zeta^3}{4}$	$1-\frac{\zeta}{4}+\frac{\zeta^2}{8}$	0.201	0.312
bcc	$\frac{1}{2}(1+\sqrt{1-\frac{20}{3}\zeta^2})$	1	0.237	0.375
fcc	$1-3\zeta^2+\frac{\zeta^3}{2}$	$1-\frac{\zeta}{2}+\frac{\zeta^2}{4}$	0.136	0.25

where $\tilde{g}(\zeta)$ is some unknown function describing the effective broadening of the ranges of localization of neighbors of the central atom 0 due to the correlative interaction with surrounding atoms. Next we integrate f_{z+1} over the coordinates of atoms of the cell, except 0 and 1, with the x axis passing through the sites 0 and 1. The resulting two-particle function $f_2(\mathbf{q}_0,\mathbf{q}_1)$ should be symmetric with respect to variables $\mathbf{q}_0$ and $\mathbf{q}_1$. As a result, the distribution function of two neighboring atoms 0 and 1 is given by

$$\begin{aligned} f_2(\mathbf{q}_0,\mathbf{q}_1) = C_2\exp\{-\gamma[&g_l(\zeta)(x_0^2+x_1^2)-2\zeta\chi(\zeta)x_0x_1 \\ &+g_t(\zeta)(y_0^2+y_1^2+z_0^2+z_1^2)]\}, \end{aligned} \tag{9}$$

where the functions $g_l(\zeta)$ and $g_t(\zeta)$ describe the effective broadening of atomic distributions in longitudinal and transverse directions, and $\chi(\zeta)\leqslant 1$ determines a damping of interatomic correlations by the surrounding. A term responsible for an effective transverse correlation is omitted in Eq. (9) because it is negligible.

Since the one-particle function f_1 of the distribution of displacements should be symmetric with respect to coordinates of the atom, the functions $g_l(\zeta)$ and $g_t(\zeta)$ are related to each other as

$$g_t(\zeta)=g_l(\zeta)\left[1-\left(\frac{\zeta\chi(\zeta)}{g_l(\zeta)}\right)^2\right].$$

Results of calculation of functions $g_l(\zeta)$ and $\chi(\zeta)$ for various types of crystals are listed in Table I. The two-dimensional crystals are assumed to possess the triangular lattice. In the same table we show the limit values ζ_0 and $\zeta_{\rm H}$ of the correlation parameter, found from Eq. (5) in the cases of zero and high temperatures $[T\gg\hbar\omega_j(\mathbf{k})]$, respectively, which are determined only by the lattice geometry and are independent of specific values of atomic mass and constant of the quasielastic bond.

If atoms n and n' are not neighboring, the correlations between their displacements are negligible. We consider their binary distribution function to be just a product of the one-particle functions,

$$f_2(\mathbf{q}_n,\mathbf{q}_{n'})=f_1(\mathbf{q}_n)\,f_1(\mathbf{q}_{n'}), \tag{10}$$

where

$$f_1(\mathbf{q}_n)=C_1\exp[-\gamma g_t(\zeta)q_n^2]. \tag{11}$$

III. FREE ENERGY

In the present section we evaluate the free energy F of a simple perfect crystal with pairwise interaction using the model of the binary functions of the atomic distribution. We proceed from the Gibbs-Bogoliubov inequality

$$F \leqslant F_H = F_0 + \langle U - U_0 \rangle, \tag{12}$$

where U is the potential energy of the crystal, $\langle \cdots \rangle$ is an average over the states of the harmonic crystal, and

$$F_0 = T \sum_{\mathbf{k},j} \ln\left[2\sinh\left(\frac{\hbar\omega_j(\mathbf{k})}{2T}\right)\right], \tag{13}$$

$$\langle U_0 \rangle = \frac{1}{4} \sum_{\mathbf{k},j} \hbar\omega_j(\mathbf{k}) \coth\left(\frac{\hbar\omega_j(\mathbf{k})}{2T}\right) \tag{14}$$

are the free energy and average potential energy of a harmonic crystal, respectively. The average potential energy of the crystal is calculated using the binary distribution functions of atomic displacements of the simple crystal given by Eq. (9) or (10) and is expressed as

$$\begin{aligned} \langle U \rangle &= \frac{1}{2} \sum_{n,n'} \langle u(r_{nn'}) \rangle \\ &= \frac{1}{2} \sum_{n,n'} \int u(r_{nn'}) f_2(\mathbf{q}_n, \mathbf{q}_{n'}) d\mathbf{q}_n d\mathbf{q}_{n'}, \end{aligned} \tag{15}$$

where $u(r)$ is interatomic potential, $n \neq n'$.

Using the symmetric binary functions (9) and (10) for the evaluation of $\langle U \rangle$ results in omitting the odd derivatives of the interatomic potential, which are of particular importance at high temperatures. The leading contribution to the free energy due to cubic anharmonicity was taken into account by perturbation theory in the ISC approximation,[11] which represents the first-order SCP theory corrected for the cubic terms. The ISC theory is known to give an excellent description of the thermodynamic properties of the quasiclassical anharmonic solids (Ar, Kr, and Xe),[11,20] though results for solid neon do not fit satisfactorily the observed data at high temperature.[21] Similarly to the ISC model,[11] we add a correction ΔF_3 due to the cubic anharmonicity of atomic vibrations to the free energy (12) of the quasiharmonic crystal:

$$\Delta F_3 = -\frac{\hbar^2}{3N^2M^3} \sum_{1,2,3} \frac{\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)}{\omega_1\omega_2\omega_3} |\Psi_{123}|^2 W_{123}, \tag{16}$$

where

$$\begin{aligned} W_{123} = &\frac{n_1n_2 + n_2n_3 + n_3n_1 + n_1 + n_2 + n_3 + 1}{\omega_1 + \omega_2 + \omega_3} \\ &+ 3\frac{n_2n_3 + n_3n_1 - n_1n_2 + n_3}{\omega_1 + \omega_2 - \omega_3}, \end{aligned}$$

$$\Psi_{123} = \sum_{n,\alpha,\beta,\gamma} e^{i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\mathbf{R}_n/2} S_\alpha^{(1)} S_\beta^{(2)} S_\gamma^{(3)} \langle \Phi_{\alpha\beta\gamma}(0n) \rangle,$$

$S_\alpha^{(1)} = \sin(\mathbf{k}_1\mathbf{R}_n/2) e_{j_1\alpha}(\mathbf{k}_1)$, $n = (e^{\hbar\omega/T} - 1)^{-1}$, and $\langle \Phi_{\alpha\beta\gamma}(0n) \rangle$ is the third-order force constant averaged with the binary distribution function obtained in the present model. Similarly to the corresponding expression in the ISC theory,[11] the total free energy of the crystal is

$$F_T = F_H + \Delta F_3, \tag{17}$$

but here the average potential energy is calculated using the binary distribution functions taking into account the correlations between longitudinal displacements of neighboring atoms. Moreover, employment of a variational technique for the calculation of the effective constants of the quasielastic bond allows us to avoid inaccuracy due to the iteration procedure and evaluation of derivatives of the interatomic potential in the ISC model, especially at high temperature, and to get analytical expressions for thermodynamic characteristics of the crystal.

TABLE II. Parameters of the Morse and LJ potentials and the de Boer parameters Λ for the RGC's.

	Morse				LJ		
	α (Å^{-1})	A (K)	R_0 (Å)	Λ	σ (Å)	ϵ (K)	Λ_{LJ}
Ne	2.05	52.98	3.04	0.4357	2.75	40.81	0.0879
Ar	1.62	170.76	3.71	0.1360	3.37	132.52	0.0283
Kr	1.56	236.23	3.97	0.0767	3.61	182.85	0.0155
Xe	1.38	332.04	4.32	0.0457	3.92	257.34	0.0096

IV. RARE GAS CRYSTALS

A. Free energy

The simple analytic expressions for the binary distribution function (9) of atomic displacements and its coefficients (3) and (5) enables one to estimate the average potential energy of interatomic interactions for any pairwise potential. In this section we follow the method developed in the preceding sections to determine the distribution functions and equilibrium parameters for rare gas crystals with fcc lattices. As was recently shown,[24] a contribution to the cohesive energy of the RGC's due to three-body interactions does not exceed 3% for Ne and is maximal (7%) for Xe. Thus, one may use pairwise potentials to describe interatomic interactions in the RGC's. In the present work we employ the Morse potential

$$u(r) = A[e^{-2\alpha(r-R_0)} - 2e^{-\alpha(r-R_0)}]$$

and the Lennard-Jones (LJ) potential

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

where A, R_0, α, ϵ, and σ are the potential parameters. The LJ potential was recently successfully used for calculation of the properties of solid neon in the framework of the improved effective potential method.[21] The parameters of both potentials, listed in Table II, were determined so that the internal energy, lattice parameter, and (in the case of the Morse potential) the bulk modulus of the RGC's at $T=0$, calculated within the present model, fitted the observed values. In the case of the Morse potential we restrict ourselves to consideration of only the interaction of neighboring atoms, and in calculations with the LJ potential we take into account the three first coordination spheres. We also employ the only parameter β_1 of the quasielastic bond of neighboring atoms. It was found that accounting for the next constant β_2 has no pronounced effect on the calculated values of both crystal free energy and equilibrium solid-state parameters.

With the Morse potential and binary distribution function (9), the average potential energy of the interaction of neighboring atoms is expressed as

$$\frac{\langle u\rangle}{A}=\frac{e^{-2b+\frac{q}{\gamma^*}}}{1+\dfrac{2}{\gamma^* g_t\alpha R}}-\frac{2e^{-b+\frac{q}{4\gamma^*}}}{1+\dfrac{1}{2\gamma^* g_t\alpha R}}, \tag{18}$$

where $b=\alpha(R-R_0)$ is the reduced lattice expansion, $R\equiv R_1$ is the nearest-neighbor distance, $\gamma^*=\gamma/\alpha^2$, and

$$q(\zeta)=\frac{2}{g_l(\zeta)+\zeta\chi(\zeta)} \tag{19}$$

is a correlation factor, representing the contribution of the correlations in the energy of interatomic interactions ($q=2$ if $\zeta=0$). Equation (18) holds also if the atoms are not neighbors of each other, with $b_s=\alpha(R_s-R_0)$ and $q=2$. For the RGC's, it turned out that the denominators in Eq. (18) are close to unity at any temperature and pressure; i.e., the contribution of the transverse displacements of neighboring atoms to the average potential energy is negligibly small and can be omitted in the present consideration.

In the case of the LJ potential, the average potential energy of the interatomic interaction was estimated by the saddle-point technique:

$$\frac{\langle u\rangle}{4\epsilon}=\left[\left(\frac{\sigma}{R}\right)^{12}\langle\tilde{r}^{-12}\rangle-\left(\frac{\sigma}{R}\right)^{6}\langle\tilde{r}^{-6}\rangle\right],$$

where $\tilde{r}=r/R$,

$$\langle\tilde{r}^{-n}\rangle=\frac{e^{-n^2/2\tilde{\gamma}}}{\left(1-\dfrac{n}{\tilde{\gamma}}\right)^{n+1/2}}-\frac{n}{2\gamma R^2 g_t}\,\frac{e^{-(n+2)^2/2\tilde{\gamma}}}{\left(1-\dfrac{n+2}{\tilde{\gamma}}\right)^{n+5/2}},$$

and $\tilde{\gamma}=2\gamma R^2/q(\zeta)$.

It is convenient to introduce a reduced temperature $\tau=T/A$ and the de Boer parameter, which is expressed as

$$\Lambda=\frac{\hbar\alpha}{\sqrt{MA}} \tag{20}$$

in the case of the Morse potential and as

$$\Lambda_{\mathrm{LJ}}=\frac{\hbar}{\sigma\sqrt{M\epsilon}}$$

for the LJ potential.

In the subsequent consideration we present the analytical results related only to the Morse potential. If one introduces the reduced phonon frequency $\tilde{\omega}_j(\mathbf{k})$ by

$$\omega_j(\mathbf{k})=\frac{Ac\Lambda}{\hbar}\tilde{\omega}_j(\mathbf{k}), \tag{21}$$

where $c=(\beta_1/A\alpha^2)^{1/2}$ is a dimensionless parameter of the quasielastic bond of neighboring atoms, the crystal free energy depends only on the reduced temperature τ, de Boer parameter, and two variational parameters b and c, determining the lattice expansion and effective quasielastic bond constant, respectively. In all formulas containing sums over $\mathbf{k}$, we replace the summation with integration over the volume of an elementary cell of the reciprocal lattice. The computational formulas for both two- and three-dimensional rare gas crystals are summarized in Appendix B.

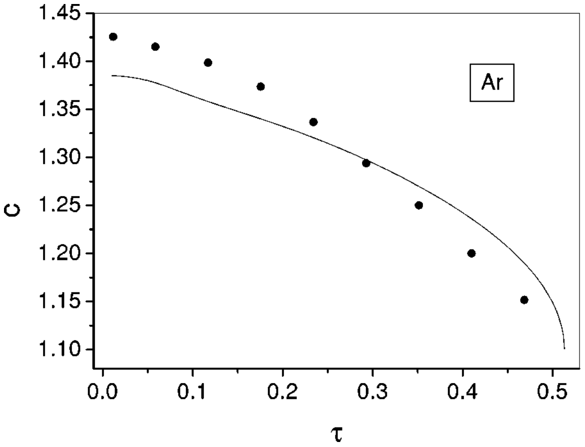

FIG. 1. Reduced effective constant of the quasielastic bond of neighboring atoms of solid Ar vs temperature at zero pressure calculated using the Morse potential by the free energy minimization (solid line) and estimated from the experimental data for the temperature dependence of the longitudinal sound velocity in the [100] direction (Ref. 25) (circles).

The equilibrium values of the variational parameters as functions of temperature are found from minimization of the free energy F_T with respect to b and c. In Fig. 1 we plot the reduced quasielastic bond parameter c versus temperature calculated for solid Ar at zero pressure. A drastic decrease of $c(\tau)$ as the temperature approaches the melting point is indicative of the vicinity of the instability point τ_c, where the crystalline system becomes unstable with respect to the quasielastic bond parameter c. For Ar, $\tau_c=0.513$, while the reduced melting temperature is 0.486. As will be shown later, the disappearance of the free energy minimum with respect to c is responsible for a steep increase of the heat capacity C_p and reduction of the bulk modulus of the RGC's at temperatures close to the melting point.

The temperature dependence of the reduced quasielastic bond parameter c may be directly related to the experimental data on the sound velocity $u_{j\mathbf{k}}$ in crystals. At small values of the wave vector $\mathbf{k}$, we may write $\tilde{\omega}_j(\mathbf{k})=\kappa_{j\mathbf{k}}kR$, where the coefficient $\kappa_{j\mathbf{k}}$ takes into account the polarization of the sound wave and direction of its propagation in the crystal, and get the relation between the sound velocity and parameter c,

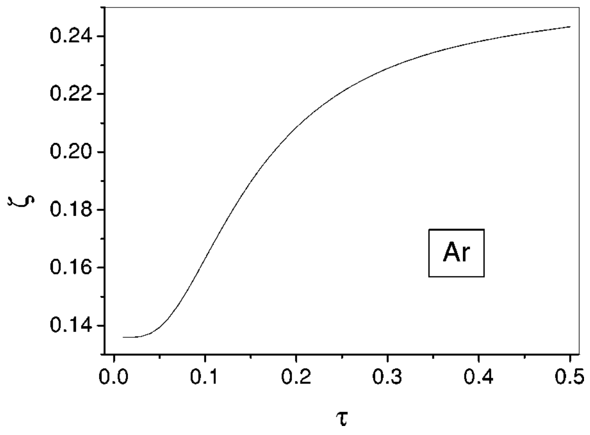

FIG. 2. Correlation parameter vs reduced temperature in Ar.

$$c(\tau)=\left(\frac{M}{\alpha^2 A}\right)^{1/2}\frac{u_{j\mathbf{k}}}{\kappa_{j\mathbf{k}}R(\tau)}.$$

In Fig. 1 we plot also the values of $c(\tau)$, found in such way from the observed temperature dependence of the longitudinal sound velocity in the [100] direction of Ar crystal.[25]

The correlation parameter ζ is one of the important characteristics of the crystalline phase as a statistical ensemble of regularly arranged particles. The temperature dependence $\zeta(\tau)$ for Ar at zero pressure calculated at equilibrium values of c is presented in Fig. 2. The correlation parameter increases continuously with temperature, compensating enhancement of the interatomic repulsion due to thermal broadening of the range of the localization of atoms. The contribution of the correlations of atomic displacements to the potential energy of interatomic interaction is expressed in Eq. (18) by the correlation factor $q(\zeta)$, which depends on the temperature through the parameter ζ (Fig. 3). As apparent from Fig. 3, the correlations affect the energy of interatomic interaction only at low temperature. At high temperature, when $\zeta\rightarrow\zeta_H$, $q(\zeta)\rightarrow 2$, coinciding with the value corresponding to the completely uncorrelated statistical distribution of displacements of atoms of the crystal.

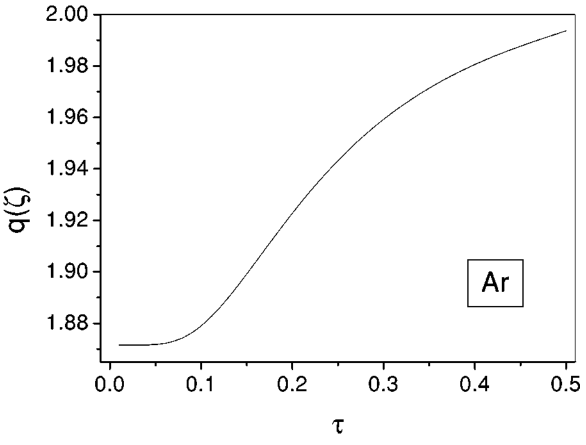

FIG. 3. Correlation factor $q(\zeta)$ vs reduced temperature in Ar.

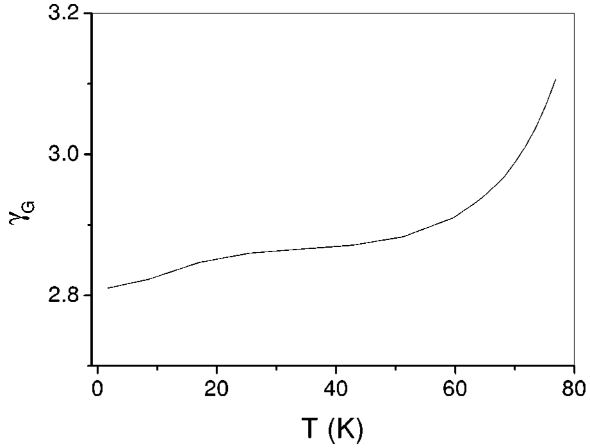

FIG. 4. The Grüneisen parameter of solid Ar vs temperature at zero pressure.

B. Equation of state of the RGC's

From Eq. (17) one can derive the equation of state of a crystal and determine its thermodynamic properties. Keeping in mind that the equilibrium value of the variational parameter c depends implicitly on the temperature and volume of the crystal, we may write the equation of state of the crystal as

$$P=P_l+\frac{E_{\mathrm{ph}}\gamma_G}{V}+\Delta P_3, \tag{22}$$

where

$$P_l=-\left(\frac{\partial\langle U\rangle}{\partial V}\right)_T-\left(\frac{\partial\langle U\rangle}{\partial c}\right)_T\left(\frac{\partial c}{\partial V}\right)_T$$

is the pressure due to the lattice compression,

$$E_{\mathrm{ph}}=-T^2\left(\frac{\partial}{\partial T}\left(\frac{F_H}{T}\right)\right)_V-\langle U\rangle$$

is the energy of the phonon subsystem of the crystal,

$$\gamma_{\mathrm{G}}=-\frac{\left(\frac{\partial\ln c}{\partial\ln V}\right)_T}{1-\left(\frac{\partial\ln c}{\partial\ln T}\right)_V} \tag{23}$$

is the Grüneisen parameter, and

$$\Delta P_3=-\left(\frac{\partial\Delta F_3}{\partial V}\right)_T-\left(\frac{\partial\Delta F_3}{\partial c}\right)_T\left(\frac{\partial c}{\partial V}\right)_T$$

is an additional contribution to the phonon gas pressure due to cubic anharmonicity (phonon interaction).

In Fig. 4 we plotted the calculated temperature dependence of the Grüneisen parameter for Ar, which exhibits an anomalous increase in the vicinity of the melting point.

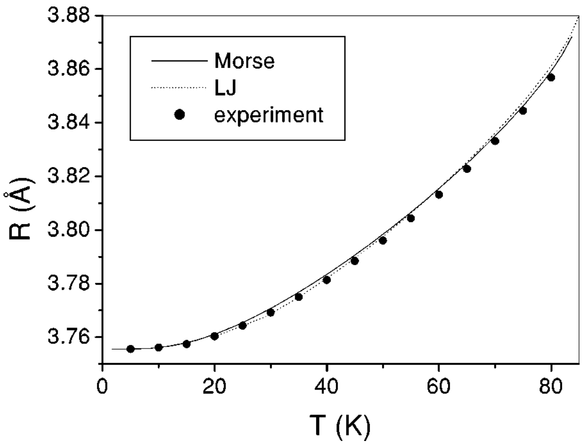

FIG. 5. Temperature dependence of the nearest-neighbor distance in solid Ar at zero pressure. The observed values are from Ref. 26.

In Figs. 5–7 we show the thermodynamic properties of solid Ar (nearest-neighbor distance, heat capacity, and bulk modulus) versus temperature, calculated in the framework of the present approach.

C. Rare gas crystals at high and low temperatures

In both limiting cases of high and low temperatures, the expressions for γ^*, ζ, $\varphi_s=(F_0-\langle U_0\rangle)/NA$, and $\varphi_3=\Delta F_3/NA$ may be expanded into power series with respect to the parameter $c\Lambda/\tau$. Such an expansion simplifies substantially the minimization of the free energy with respect to b and c and allows one to get explicit analytical expressions for the equilibrium parameters of the crystal.

In the high-temperature limit $\tau > c\Lambda$, we find

$$\gamma^* \approx \frac{c^2}{\tau}\sum_{l=0}^{3} n_l\left(\frac{c\Lambda}{\tau}\right)^{2l}, \tag{24}$$

$$\zeta \approx m_0 + m_1\left(\frac{c\Lambda}{\tau}\right)^2, \tag{25}$$

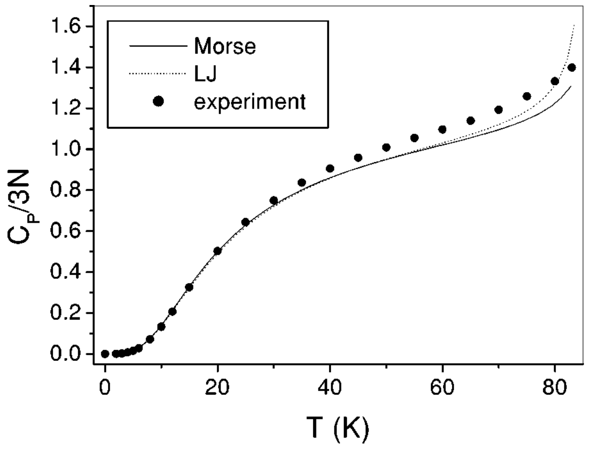

FIG. 6. Heat capacity of solid Ar per atom vs temperature at zero pressure. The observed values are from Ref. 27.

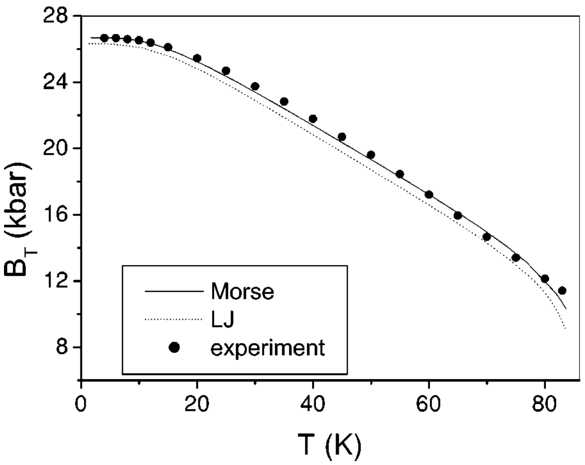

FIG. 7. Zero-pressure bulk modulus of solid Ar per atom vs temperature at zero pressure. The observed values are from Ref. 26.

$$\varphi_s \approx \tau\left[p_0 + p_1\left(\frac{c\Lambda}{\tau}\right)^4\right] + 3\tau\ln\left(\frac{c\Lambda}{\tau}\right), \tag{26}$$

$$\varphi_3 \approx -\frac{a_3\tau^2}{c^6}\left(e^{-2b+q/\gamma^*} - \frac{1}{4}e^{-b+q/4\gamma^*}\right)^2, \tag{27}$$

where $a_3 \approx 1.5$ for Ar, and n_l, m_l, and p_l are numerical coefficients determined by the phonon spectrum of the crystal (see Appendix C). Values of these coefficients for the fcc lattice are listed in Table III.

In the case of low temperature ($\tau \ll c\Lambda$),

$$\gamma^* \approx \frac{c}{\Lambda}\left[s_1 - s_2\left(\frac{\tau}{c\Lambda}\right)^4\right], \tag{28}$$

$$\varphi_s \approx c\Lambda\left[t_1 - t_2\left(\frac{\tau}{c\Lambda}\right)^4\right], \tag{29}$$

and the correlation parameter at $T=0$ is $\zeta_0=0.136$. Expressions for the coefficients s_l and t_l are given in Appendix C, and their values for the fcc lattice are shown in Table IV.

In the case of zero temperature, the internal energy per atom is given by

$$E_0 = -6A\exp\left(-\frac{1}{2s_1}\frac{q_0\Lambda}{c_0}\right) + \frac{3}{4}A\Lambda s_1 c_0, \tag{30}$$

where

$$c_0 = \sqrt{\frac{3q_0}{t_1 s_1}} - \frac{q_0}{4s_1}\Lambda \tag{31}$$

TABLE III. Coefficients of the high-temperature expansion of the parameters γ^*, ζ, and φ_s.

n_0	n_1	n_2	n_3	m_0	m_1	p_0	p_1
2	5/6	0.475	0.296	1/4	−7/96	1/3	1/48

TABLE IV. Coefficients of the low-temperature expansion of the parameters γ^* and φ_s.

s_1	s_2	t_1	t_2
1.928	0.550	1.446	0.092

is the equilibrium parameter of the quasielastic bond at $T=0$, $q_0=q(\zeta_0)=1.87$. The equilibrium quantum lattice expansion is

$$b_0=\frac{3}{4s_1}\frac{q_0\Lambda}{c_0}. \tag{32}$$

The average distance between neighboring atoms and the bulk modulus of the crystal at $T=0$ are, respectively, given by

$$R(0)=R_0+\frac{b_0}{\alpha}, \tag{33}$$

$$B_T(0)=\frac{4\sqrt{2}A\alpha^2e^{-2b_0/3}}{3R(0)}\left[1-\frac{9}{8s_1}\frac{\dfrac{q_0\Lambda}{c_0}}{1+\dfrac{7}{8s_1}\dfrac{q_0\Lambda}{c_0}}\right]. \tag{34}$$

Equating the right-hand parts of Eqs. (30), (33), and (34) to the observed values of the sublimation energy, lattice spacing, and bulk modulus for the RGC's (see Ref. 28 and references therein), we obtained a set of equations for three parameters of the Morse potential. In the case of the LJ potential, we fitted the crystal energy and the interatomic distance at $T=0$.

Consideration of the purely quantum motion of atoms of the crystal in the limit $T=0$ may be used as a check of the validity of the present statistical model of solids. On the one hand, equilibrium values of the parameters γ and ζ at $T=0$ can be found directly from Eqs. (3) and (5). On the other hand, they may be considered as variational parameters of the ground-state wave function of atoms of the crystal. In this case, values of γ and ζ can be calculated by the direct variational method from the corresponding Scrödinger equation. The ground-state energy of the crystal as a function of γ^* and ζ is

$$E(\gamma,\zeta)=NA\left(\frac{3}{4}\gamma^*\Lambda^2-6e^{-q(\zeta)/2\gamma^*}\right).$$

We found that minimization of E with respect to γ^* and ζ yields the equilibrium energy and parameters of the crystal which coincide completely with the corresponding zero-temperature values calculated within the present approach.

In the limit of a classical crystal ($\Lambda=0$), its equilibrium parameters are expressed explicitly as

$$b\approx\frac{3\tau}{4c^2},$$
$$c\approx(1+\sqrt{1-\tau/\tau_c})^{1/2}, \tag{35}$$

where the critical temperature $\tau_c\approx(1+9a_3/16)^{-1}$ corresponds to the point of the disappearance of the minimum of the free energy with respect to c. Keeping in mind the temperature dependence of the constant of the quasielastic bond (35), we can represent the crystal heat capacity in the high-temperature range as

$$\frac{C_p}{3N}\approx1+\frac{\tau}{2c^4}+\frac{\tau^2}{4c^6\tau_c^2\sqrt{1-\tau/\tau_c}}. \tag{36}$$

It follows from Eq. (36) that the anomalous rise of the heat capacity C_p near the melting point is associated with an increasing of the temperature sensitivity of the effective parameter of the quasielastic bond ($|dc/d\tau|\gg1$) as the temperature approaches the instability point τ_c. Numerical analysis of the instability temperature for the RGC's shows that τ_c is slightly higher than the melting point τ_M, but $|dc/d\tau|\gg1$ at $\tau=\tau_M$.

V. DISCUSSION

The starting point of the method of statistical description of the crystal state, developed in the present work, is the common representation of a crystal as a system of bound oscillators, whose collective motion is described by a set of normal modes of vibration. From such a consideration, we passed on consistently to the representation of the crystal as an ordered ensemble of particles, whose spatial distribution is determined by the dynamical characteristics of the crystal. Appealing to symmetry reasoning allowed us to reduce the N-particle function of the distribution of atomic displacements (4) to the binary distribution function (9), providing a means for the exact evaluation of the average potential energy (15) of the pair interaction of atoms in the crystal. Introducing the effective constant of the quasielastic bond, we parametrized the crystal free energy (17), representing it as a function of the reduced temperature τ, the De Boer constant, and two dimensionless variational parameters, the lattice expansion and the constant of the quasielastic bond. In contrast to the iterative procedure employed in the SCP theories, within the present model the equilibrium values of the variational parameters are calculated via minimization of the crystal free energy. Such an approach not only gives the benefit of simple and clear computations (which become trivial in the cases of high and low temperatures), but allows one to reveal a number of characteristic features, which are not evident within the SCP model.

An analysis of the free energy of the RGC as a function of the effective parameter of the quasielastic bond shows that the free energy minimum with respect to c disappears at a temperature τ_C just above the melting point τ_M. The approach to the instability point is accompanied by a steep reduction of the parameter c ($|dc/d\tau|\gg1$ at $\tau\approx\tau_C$) in a narrow temperature range (Fig. 1). Such drastic change of the sensitivity of the system manifests itself in an abrupt increase of the heat capacity C_p of the RGC's near the melting point (Fig. 6), which was observed experimentally. Such behavior of the RGC is attributed to the substantial contribution of the anharmonicity to the free energy of the crystal in the high-temperature range, depending strongly on c at $\tau > c\Lambda$. The vibrational anharmonicity leads to a breakdown of the self-consistent quasielastic interatomic bonds at high temperatures, manifesting itself in the disappearance of the free energy minimum with respect to c. A correlation between this instability and melting of the RGC's is the subject of a separate study. Particularly, it was demonstrated[29] that the cubic anharmonicity of atomic vibrations is responsible for a dramatic reduction of the vacancy formation energy near the melting temperature.

Another item to be mentioned is the role of the interatomic correlations in the statistical model of the crystal. As apparent from Fig. 2, the correlation parameter ζ rises with temperature. But the least value of the correlation factor $q(\zeta)$, providing the maximal gain in the energy of the interatomic interaction, is realized at low temperature (Fig. 3). At high temperature $q(\zeta)\rightarrow 2$, which coincides with the value $q(0)=2$ corresponding to the completely uncorrelated system. However, taking the temperature dependence of the factor q into account is important in the calculation of the heat capacity and bulk modulus of solids.

In the present work we studied the thermodynamics of the RGC's, using two potentials to approximate the interatomic interaction. The parameters of both potentials were found by fitting the observed values of the internal energy, interatomic distance, and bulk modulus of the RGC's at $T=0$ in the framework of the present statistical model of the solid state. Comparison of the theoretical temperature dependences of the lattice spacing, heat capacity, and bulk modulus of the RGC, calculated for both potentials, with the experimental data over the whole range of allowable temperatures (Figs. 5–7), displays good agreement between the theoretical and observed results.

In conclusion, it should be noted that the present model may be rather efficient in the investigation of the thermodynamic state of crystals with complex lattices.

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APPENDIX A: CALCULATION OF THE *N*-PARTICLE DISTRIBUTION FUNCTION

Let us determine the Fourier transform of the thermodynamic probability density $P(X_j(\mathbf{k}))$ of a real normal coordinate $X_j(\mathbf{k})$ as

$$\sigma_{\mathbf{k},j}(g)=\int_{-\infty}^{\infty}P(X_j(\mathbf{k}))e^{igX_j(\mathbf{k})}dX_j(\mathbf{k}). \tag{A1}$$

Then the Fourier inversion gives

$$P(X_j(\mathbf{k}))=\frac{1}{2\pi}\int_{-\infty}^{\infty}\sigma_{\mathbf{k},j}(g)e^{-igX_j(\mathbf{k})}dg. \tag{A2}$$

In view of the definition of $P(X_j(\mathbf{k}))$, Eq. (A1) can be rewritten as

$$\sigma_{\mathbf{k},j}(g)=\langle e^{igX_j(\mathbf{k})}\rangle, \tag{A3}$$

where $\langle\cdots\rangle$ denotes averaging over the equilibrium distribution of $X_j(\mathbf{k})$. In terms of the operators $b_{\mathbf{k},j}$ and $b^{\dagger}_{\mathbf{k},j}$ of the creation and annihilation of phonons, we may write

$$X_j(\mathbf{k})=\frac{1}{2}\left(\frac{\hbar}{2\omega_j(\mathbf{k})}\right)^{1/2}[b_{\mathbf{k},j}+b^{\dagger}_{\mathbf{k},j}+b_{-\mathbf{k},j}+b^{\dagger}_{-\mathbf{k},j}], \tag{A4}$$

where $\omega_j(\mathbf{k})$ is the phonon frequency, corresponding to the wave vector $\mathbf{k}$ and jth vibration branch. The average (A3) can be expressed in terms of cumulants K_n of the random variable $X_j(\mathbf{k})$ as

$$\langle e^{igX_j(\mathbf{k})}\rangle=\exp\left(\sum_{n=1}^{\infty}\frac{K_n}{n!}\right).$$

Restricting ourselves to the first nonvanishing cumulant

$$K_2=-g^2\langle X_j^2(\mathbf{k})\rangle=-\frac{g^2\hbar}{2\omega_j(\mathbf{k})}\left(n_{\mathbf{k}j}+\frac{1}{2}\right),$$

where $n_{\mathbf{k}j}=[\exp(\hbar\omega_j(\mathbf{k})/T-1)]^{-1}$ is the average occupation number of phonons, we obtain

$$\sigma_{\mathbf{k},j}(g)=\exp\left[-\frac{g^2\hbar(n_{\mathbf{k}j}+1/2)}{4\omega_j(\mathbf{k})}\right]. \tag{A5}$$

Substituting Eq. (A5) into Eq. (A2), we get

$$P(X_j(\mathbf{k}))=C\exp\left[-\frac{2\omega_j(\mathbf{k})}{\hbar}\tanh\left(\frac{\hbar\omega_j(\mathbf{k})}{2T}\right)X_j^2(\mathbf{k})\right].$$

In a similar way one can calculate the probability density $P(Y_j(\mathbf{k}))$ of the variable $Y_j(\mathbf{k})$. In the representation of normal modes, the crystal distribution function f_N is a product of probability densities of $3N$ independent variables $X_j(\mathbf{k})$ and $Y_j(\mathbf{k})$ or the square root of the product of probability densities of *all* real normal coordinates,

$$f_N=C\exp\left[-\sum_{\mathbf{k},j}\frac{\omega_j(\mathbf{k})}{\hbar}\tanh\left[\frac{\hbar\omega_j(\mathbf{k})}{2T}\right][X_j^2(\mathbf{k})+Y_j^2(\mathbf{k})]\right],$$

where the summation is taken over all wave vectors in the first Brillouin zone. Taking into account that

$$X_j^2(\mathbf{k})+Y_j^2(\mathbf{k})=\frac{M}{N}\sum_{nn'\beta\beta'}q_{n\beta}q_{n'\beta'}e_{j\beta}(\mathbf{k})e_{j\beta'}(\mathbf{k})\cos\mathbf{k}(\mathbf{R}_n-\mathbf{R}_{n'}),$$

we rewrite f_N in the coordinate representation

$$f_N=\exp\left[-\frac{M}{N\hbar}\sum_{nn'\beta\beta'}q_{n\beta}q_{n'\beta'}\sum_{\mathbf{k},j}\ \omega_j(\mathbf{k})\right.$$
$$\left.\times\tanh\left(\frac{\hbar\omega_j(\mathbf{k})}{2T}\right)e_{j\beta}(\mathbf{k})e_{j\beta'}(\mathbf{k})\cos\mathbf{k}(\mathbf{R}_n-\mathbf{R}_{n'})\right].$$

APPENDIX B: COMPUTATIONAL FORMULAS FOR THE RARE GAS CRYSTALS

To carry out integration over the volume of an elementary cell of the reciprocal lattice, we introduce reduced variables **K** proportional to the coefficients of decomposition of the wave vector **k** with respect to the vectors of the reciprocal lattice. Integration is to be made over each variable K_i from 0 to 1. For the two-dimensional triangular lattice with the x axis directed along a chain of neighboring atoms, such variables are given by

$$k_xR=2\pi K_1,\quad k_yR=2\pi(2K_2-K_1)/\sqrt{3}.$$

For the bcc lattice with the coordinate axes lying in the [100], [010], and [001] directions,

$$k_xR=\sqrt{3}\pi(K_1+K_3),$$
$$k_yR=\sqrt{3}\pi(K_1+K_2),$$
$$k_zR=\sqrt{3}\pi(K_2+K_3),$$

and for the fcc lattice with the same orientation of the coordinate axes,

$$k_xR=\sqrt{2}\pi(K_1-K_2+K_3),$$
$$k_yR=\sqrt{2}\pi(K_1+K_2-K_3),$$
$$k_zR=\sqrt{2}\pi(-K_1+K_2+K_3).$$

Equations (3), (5), (13), and (14) take on the form

$$\gamma^*=\frac{c}{\Lambda}\sum_j\int\tilde{\omega}_j(\mathbf{K})\tanh\left[\frac{c\Lambda\tilde{\omega}_j(\mathbf{K})}{2\tau}\right]e_{jx}^2(\mathbf{K})d\mathbf{K},\quad\text{(B1)}$$

$$\zeta=-\frac{c}{\Lambda\gamma^*}\sum_j\int\tilde{\omega}_j(\mathbf{K})\tanh\left[\frac{c\Lambda\tilde{\omega}_j(\mathbf{K})}{2\tau}\right]e_{jx}^2(\mathbf{K})\cos\eta d\mathbf{K},\quad\text{(B2)}$$

$$\frac{F_0}{NA}=\tau\sum_j\int\ln\left\{2\sinh\left[\frac{c\Lambda\tilde{\omega}_j(\mathbf{K})}{2\tau}\right]\right\}d\mathbf{K},\quad\text{(B3)}$$

$$\frac{\langle U_0\rangle}{NA}=\frac{c\Lambda}{4}\sum_j\int\tilde{\omega}_j\coth\left[\frac{c\Lambda\tilde{\omega}_j(\mathbf{K})}{2\tau}\right]d\mathbf{K},\quad\text{(B4)}$$

where $\eta=2\pi K_1$ for triangular and fcc lattices and $\eta=2\pi(K_1+K_2+K_3)$ for the bcc lattice.

APPENDIX C: COEFFICIENTS OF THE HIGH- AND LOW-TEMPERATURE EXPANSIONS

Coefficients of the high-temperature expansions (24)–(27) and low-temperature expansions (28)–(29) are given by

$$n_0=\frac{1}{2}\sum_j\int\tilde{\omega}_j^2e_{jx}^2(\mathbf{K})d\mathbf{K},$$

$$n_1=\frac{1}{24}\sum_j\int\tilde{\omega}_j^4(\mathbf{K})e_{jx}^2d\mathbf{K},$$

$$n_2=\frac{1}{240}\sum_j\int\tilde{\omega}_j^6(\mathbf{K})e_{jx}^2d\mathbf{K},$$

$$n_3=\frac{17}{40320}\sum_j\int\tilde{\omega}_j^8(\mathbf{K})e_{jx}^2d\mathbf{K},$$

$$m_0=-\frac{1}{2n_0}\sum_j\int\tilde{\omega}_j^2(\mathbf{K})e_{jx}^2(\mathbf{K})\cos\eta d\mathbf{K},$$

$$m_1=\frac{1}{n_0}\left[m_0n_1-\frac{1}{24}\sum_j\int\tilde{\omega}_j^4(\mathbf{K})e_{jx}^2(\mathbf{K})\cos\eta\, d\mathbf{K}\right],$$

$$p_1=-\frac{3}{2}+\sum_j\int\ln\tilde{\omega}_j(\mathbf{K})\,d\mathbf{K},$$

$$p_2=\frac{1}{2880}\sum_j\int\tilde{\omega}_j^4(\mathbf{K})d\mathbf{K},$$

$$s_1=\sum_j\int\tilde{\omega}_j(\mathbf{K})e_{jx}^2(\mathbf{K})d\mathbf{K},$$

$$s_2=2\sum_j\int\tilde{\omega}_j(\mathbf{K})e^{-\tilde{\omega}_j}e_{jx}^2(\mathbf{K})d\mathbf{K},$$

$$\zeta_0=-\frac{1}{s_1}\sum_j\int\tilde{\omega}_j(\mathbf{K})\cos\eta e_{jx}^2(\mathbf{K})d\mathbf{K},$$

$$t_1=\frac{1}{4}\sum_j\int\tilde{\omega}_j(\mathbf{K})d\mathbf{K},$$

$$t_2=\sum_j\int\left[1-\frac{\tilde{\omega}_j(\mathbf{K})}{2}\right]e^{-\tilde{\omega}_j}d\mathbf{K}.$$

[*] Electronic address: akaras@imp.kiev.ua

[†] Electronic address: vilu@imp.kiev.ua

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