PHYSICAL REVIEW E **71**, 051102 (2005)

Statistical theory of noble-gas crystals and the phenomenon of sublimation

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(Received 26 August 2004; revised manuscript received 15 November 2004; published 10 May 2005)

We propose a consistent (without any fitting parameters) statistical theory of classical noble-gas crystals with pair interaction between atoms. Using the equation for the single-particle distribution function of the statistical system, we demonstrate the existence of an infinite number of exact sum rules for the amplitudes of the space-periodic solutions. Even the first sum rule leads to the solution which turns into the exact one at the absolute zero temperature. For the pair distribution function, we obtained the physically correct solution using the well-known exact relation for the compressibility as the self-consistent condition. As a result, we succeeded in recovering the equation of state of the crystal, and starting from the Lennard-Jones potential with the "gaseous" parameters, we calculated the temperature dependencies of the lattice constant and the isothermal compressibility of the crystal at the sublimation line. These calculations (including the form of the sublimation line itself) agree rather well with the corresponding experimental data for the argon-type media in the "classical" temperature region. The question about the bifurcation of the solutions is considered. Ways to further develop the theory are discussed.

DOI: 10.1103/PhysRevE.71.051102 PACS number(s): 05.20.Gg, 64.10.+h, 64.70.Dv

I. INTRODUCTION

Creating a consistent theory of freezing-melting for actual three-dimensional (3D) media is one of the outstanding problems of statistical physics (see, for example, [1] and [2]). The investigation of this problem encounters two difficulties of principle. In the first place, it is necessary to be able to describe a crystal by the fundamental equations of statistical mechanics starting from the knowledge of interatomic potential. In the second place, for the description of the crystal-liquid transition, one needs to know the thermodynamic functions of the liquid. During recent decades, some general relations for the thermodynamic functions of real condensed media have been established [3] and the theory of liquids experienced impetuous development either on the analytical level or in the field of computer simulations (see, for example, [4–6] and [7]). Nevertheless, the construction of the melting-freezing phase diagram for the actual systems requires rather laborious numerical calculations.

Beginning from Kirkwood and Monroe [8], the freezing-melting transition was considering in the context of the bifurcation phenomenon, i.e., the appearance (disappearance) of periodic solutions for the atomic density function of a statistical system (see, for example, [9–11]). However, the question about the connection between the bifurcation point and the temperature of freezing-melting of actual media was left open [12].

At present, one of the most constructive approaches to the description of the liquid-solid transition is based on different versions of the density-functional theory (see, for example, [13]), which has been adapted to the problem of freezing by Ramakrishnan and Yussouff [14]. The theory operates only with the one-particle density of the condensed matter but needs definite information concerning the binary correlations in it. Such information, in fact, is entirely extracted from the correlation characteristics of the liquid state assumed to be known from the experimental data or model calculations.

In order to obtain analytic results in the density-functional theory of freezing, its modification, known as "the fundamental measure density-functional theory," has been proposed [15] (see also, for example, [16,17]). In this case, the correlations in the fluid mixture of hard spheres are expressed through the characteristic (weight) functions for the geometry of the individual spheres.

Thus, in most cases the problem of freezing was analyzed either in the framework of the model of hard spheres (as in [16]) or by the use of some additional suppositions about the form of the pair distribution function in the crystal phase (as in Refs. [8,13,14,18–21]). In this situation, the construction of a quantitative theory of freezing on the basis of some realistic interatomic potential and without the use of any *ad hoc* assumptions on the form of the correlation functions in the crystal phase is the actual problem of fundamental physics.

Although, in view of the above-mentioned difficulties, the general approach to the theory of freezing-melting seems too complicated, one can point out the natural domain relating to the sublimation part of the phase diagram where the second of the difficulties does not arise. While there are enough extensive experimental data for this domain, in particular concerning the thermodynamic properties of the noble-gas crystals (see, for example, Refs. [22–26]), a consistent theoretical interpretation of the sublimation phenomenon has been absent up to now. It is important to note that no theory of sublimation could, in principle, be constructed in the framework of the above-mentioned approaches based on the hard-sphere model.

In the present paper, we offer a consistent (without any fitting parameters) theory of sublimation of the noble-gas crystals. In Sec. II, being based on the classical equations for the partial distribution functions of the system with pair interaction between atoms, we find a physically correct func-

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tional form of the pair function for the crystal phase. Section III is devoted to a presentation of the equation for the singlet function in a form demonstrating the existence of an infinite number of exact sum rules which essentially facilitate the determination of suitable spatially periodic solutions. The problem becomes completely closed if one uses the well-known relation for the isothermal compressibility of the system. In Sec. IV, the self-consistent equations are solved analytically in the low-temperature limit, and the low-temperature dependencies of the thermodynamic functions of the Lennard-Jones crystal are found. Then (Sec. V), the expression for the crystal entropy in the main approximation is obtained and the sublimation curve is derived. Section VI contains the results of numerical solution of the derived equations. In Sec. VII, we demonstrate the applicability of the theory for a quantitative description of the thermodynamic characteristics of the Lennard-Jones crystal near the "classical" domain of the sublimation line. We also discuss different sides of the proposed theory and outline some ways to develop it further. Finally, in Sec. VIII, a brief summary of the obtained results is given.

II. BASIC ASPECTS OF THE THEORY

Following Kirkwood and Monroe [8], the crystal phase can be described by a spatially periodic singlet distribution function $f(\mathbf{r})$ bearing the information about the local density of atoms at an arbitrary point $\mathbf{r}$. $f(\mathbf{r})$ satisfies the first equation of the BBGKY hierarchy (see, for example, Refs. [27,12,28–30]) for the partial distribution functions,

$$T\,\nabla f(\mathbf{r}) + n_0 \int f(\mathbf{r},\mathbf{r}')\,\nabla W(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \mathbf{0}, \qquad (1)$$

where n_0 is the average number of atoms per unit volume of the system; the energy of pair interaction of atoms $W(|\mathbf{r}-\mathbf{r}'|)$ is assumed to depend on the distance between the particles, the centers of which are at points $\mathbf{r}$ and $\mathbf{r}'$. Equation (1) connects $f(\mathbf{r})$ with the pair function $f(\mathbf{r},\mathbf{r}')=f(\mathbf{r}',\mathbf{r})$ which satisfies the equation

$$T\,\nabla f(\mathbf{r},\mathbf{r}') + f(\mathbf{r},\mathbf{r}')\,\nabla W(|\mathbf{r}-\mathbf{r}'|) + n_0 \int f(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,\nabla W(|\mathbf{r} - \mathbf{r}''|)d\mathbf{r}'' = \mathbf{0}, \qquad (2)$$

where $f(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ is the triplet correlation function symmetrical with respect to its arguments. The partial functions are normalized by the conditions $V^{-1}\int f(\mathbf{r})d\mathbf{r}=1$, $V^{-1}\int f(\mathbf{r},\mathbf{r}')d\mathbf{r}'=f(\mathbf{r})$, etc., where V is the volume (macroscopic) of the system.

For the argonlike systems of interest (including their crystal state), $W(|\mathbf{r}-\mathbf{r}'|)$ can be well approximated by the Lennard-Jones potential [12,31,32]

$$W(|\mathbf{r}-\mathbf{r}'|) = 4w_0\hat{W}(|\mathbf{r}-\mathbf{r}'|),$$

$$\hat{W}(|\mathbf{r}-\mathbf{r}'|) = \left[\left(\frac{|\mathbf{r}-\mathbf{r}'|}{D}\right)^{12} - \left(\frac{|\mathbf{r}-\mathbf{r}'|}{D}\right)^{6}\right], \qquad (3)$$

where w_0 and D are the parameters scaling the energy and the distance, respectively. As it is known [31,32], potential (3) with w_0 and D values determined from the experimental data for the rare noble gases can be used for the quantitative description of many characteristics (the lattice constants, the cohesive energies, etc.) of the van der Waals crystals. So, constructing the theory, we will use Eq. (3) with these (known from the gas measurements) values of the parameters.

In the fluid state, $f(\mathbf{r})=1$ and $f(\mathbf{r},\mathbf{r}')$ depends on $|\mathbf{r}-\mathbf{r}'|$ only [12,27,28]. But in the crystal case, $f(\mathbf{r})$ as well as $f(\mathbf{r},\mathbf{r}')$, etc., are the spatially periodic functions, i.e., for any lattice period $\mathbf{a}$ it must be $f(\mathbf{r}+\mathbf{a})=f(\mathbf{r})$, $f(\mathbf{r}+\mathbf{a},\mathbf{r}'+\mathbf{a})=f(\mathbf{r},\mathbf{r}')$, etc. Obviously, in the perfectly ordered state (in the absence of intrinsic defects, i.e., at $T=0$),

$$f(\mathbf{r}) = \frac{1}{n_0}\sum_{\mathbf{a}} \delta(\mathbf{r}-\mathbf{a}), \qquad (4)$$

where the sum of Dirac's δ functions is carried out upon all (including the trivial $\mathbf{a}=\mathbf{0}$) lattice periods.

In what follows, it is convenient to present

$$f(\mathbf{r},\mathbf{r}') = f(\mathbf{r})f(\mathbf{r}')B(\mathbf{r},\mathbf{r}'),$$

$$f(\mathbf{r},\mathbf{r}',\mathbf{r}'') = f(\mathbf{r})f(\mathbf{r}')f(\mathbf{r}'')B(\mathbf{r},\mathbf{r}',\mathbf{r}''), \qquad (5)$$

where the new pair function $B(\mathbf{r},\mathbf{r}')$ and the triplet function $B(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ must tend to unity when the interparticle distances increase [27] and also in the crystal state $B(\mathbf{r}+\mathbf{a},\mathbf{r}'+\mathbf{a})=B(\mathbf{r},\mathbf{r}')$, etc. Below we put $B(\mathbf{r},\mathbf{r}')\equiv B(\mathbf{r}-\mathbf{r}')$ (this form is necessarily invariant under the translations). Representation (5) means that the main information about the periodic structure of the crystal is contained in the singlet function and one can expect that, for example, the function $B(\mathbf{r}-\mathbf{r}')$ will be close to unity at $|\mathbf{r}-\mathbf{r}'|>D$ while at lower distances it will be close to zero (impenetrability of the atoms).

The simplest way to convert Eqs. (1) and (2) into the closed-form system lies in the utilization of the well-known Kirkwood's superposition approximation [12,28],

$$B(\mathbf{r},\mathbf{r}',\mathbf{r}'') = B(\mathbf{r}-\mathbf{r}')B(\mathbf{r}-\mathbf{r}'')B(\mathbf{r}'-\mathbf{r}''). \qquad (6)$$

As it is known [12], this approximation is well justified for the gas phase, but for the liquid its validity is worse. However, there exists the statement (see the article by Temperley in Ref. [12]) that approximation (6) can again become good in the crystal phase. Below, we will confirm this statement finding a physically correct form of $B(\mathbf{r}-\mathbf{r}')$ suitable for quantitative description of the sublimation phenomenon of the noble-gas crystals.

The pair function in the fluid phase automatically depends on $|\mathbf{r}-\mathbf{r}'|$ irrespective of the position $\mathbf{r}'$ of the chosen particle. However, the existence of the long-range order in the crystal case forces us to ascribe some definite position to the chosen particle in the coordinate system where the crystal as a whole is at rest. It is convenient to put $\mathbf{r}'=\mathbf{0}$ in the equation for the $B(\mathbf{r}-\mathbf{r}')$ function. Then, substituting Eq. (5) into Eq.

(2) and taking into account Eq. (6) and Eq. (1), we come to the equation

$$T\boldsymbol{\nabla} B(\mathbf{r}) + B(\mathbf{r})\boldsymbol{\nabla} W(r) + n_0 B(\mathbf{r}) \int f(\mathbf{r}'')B(\mathbf{r}-\mathbf{r}'')[B(\mathbf{r}'')-1] \times \boldsymbol{\nabla} W(|\mathbf{r}-\mathbf{r}''|)d\mathbf{r}'' = 0, \tag{7}$$

where the designation $r \equiv |\mathbf{r}|$ is introduced. One can verify that at $T=0$, when the singlet function is given by Eq. (4), the solution of Eq. (7) is

$$B(\mathbf{r})|_{T=0} = \Theta(r-D'), \tag{8}$$

where $\Theta(r-D')$ is the step function, equal to unity at the positive arguments and to zero at the negative ones. Here, the constant D' must be less than the absolute value of the minimal nontrivial period 1.09 D [31,32] of the fcc crystal of interest; we will see below that $D'=D$.

Let us introduce the Fourier transform of the singlet function,

$$f_{\mathbf{k}} = \frac{1}{V}\int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}), \quad f_{-\mathbf{k}} = f_{\mathbf{k}}. \tag{9}$$

In the disordered state, $f_{\mathbf{k}}$ is zero at all $\mathbf{k}$'s except $\mathbf{k}=\mathbf{0}$: $f_{\mathbf{k}=\mathbf{0}}=1$. On the contrary, for the crystal, $f_{\mathbf{k}}$ is nonzero also at those $\mathbf{k}$'s that coincide with all possible vectors $\mathbf{b}$ (including $\mathbf{b}=\mathbf{0}$) of the nodes of the reciprocal lattice [18,31–33]. For the fcc crystals of the noble gases, the reciprocal lattice is bcc and, returning to Eq. (1), it is convenient to introduce the dimensionless vectors $\mathbf{L}=\mathbf{b}/b_0$, where b_0 is the edge length of the Bravais bcc cube. In this case, the fcc lattice constant along the cubic axis is

$$a_0 = \frac{4\pi}{b_0}, \tag{10}$$

while the connection (cf. [33])

$$n_0 = \frac{b_0^3}{16\pi^3} \tag{11}$$

is the important "closing" condition for Eq. (1). Thus, for the crystal

$$f(\mathbf{r}) = \sum_{\mathbf{L}} f_{\mathbf{L}} e^{ib_0\mathbf{L}\cdot\mathbf{r}}, \tag{12}$$

and, obviously, the amplitudes $f_{\mathbf{L}}$ depend on $L \equiv |\mathbf{L}|$.

Equations (1) and (7) have to be added by the known expression (see, for example, Refs. [12,27–30]) for the pressure p,

$$p = n_0 T - \frac{n_0^2}{6V}\int d\mathbf{r}\int d\mathbf{r}' f(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\frac{dW(|\mathbf{r}-\mathbf{r}'|)}{d|\mathbf{r}-\mathbf{r}'|} = n_0 T - \frac{n_0^2}{6}\int d\mathbf{R} B(\mathbf{R}) R \frac{dW(R)}{dR}\sum_{\mathbf{L}} f_{\mathbf{L}}^2 e^{ib_0\mathbf{L}\cdot\mathbf{R}}. \tag{13}$$

In the "gas" limit ($n_0 \to 0$), Eq. (7) has the known solution $B(\mathbf{r})=\exp[-W(r)/T]$ which, however, is too rough to be used for the analysis of the freezing problem. One can show a self-consistent procedure giving a suitable approximate solution of Eq. (7) without the assumption about the "smallness" of n_0. This procedure is based on the consideration of the formal limit of "large" r in Eq. (7), which makes it possible to expand $B(\mathbf{r}-\mathbf{r}'')$ and $W(|\mathbf{r}-\mathbf{r}''|)$ on powers of $\mathbf{r}''$ in the integrand. Restricting ourselves to the terms of order zero in the expansions, one can see that the desired solution will be spherically symmetrical and will satisfy the ordinary nonlinear differential equation of the first order,

$$T\frac{dB(r)}{dr} + B(r)[1 - YB(r)]\frac{dW(r)}{dr} = 0 \tag{14}$$

with the parameter

$$Y = n_0 \int f(\mathbf{r}'')[1 - B(r'')]d\mathbf{r}''. \tag{15}$$

Note that taking into account the subsequent terms in the expansions leads to the fact that $B(\mathbf{r})$ gains the lattice symmetry.

At $0 \leqslant Y \leqslant 1$, Eq. (14) has a continuous solution with the proper behavior at all r's. Introducing the dimensionless temperature $T^* = T/w_0$, we obtain the desired solution,

$$B(r) = \frac{1}{Y + (1-Y)\exp[4\hat{W}(r)/T^*]}. \tag{16}$$

Solution (16), taking into account Eq. (3), has the single maximum but the form of this solution at finite Y's differs from the "gaseous" one (at $Y=0$).

In principle, Eq. (15) could be used for the self-consistent determination of the parameter Y. In fact, this equation is a consequence of Kirkwood's superposition approximation. Because the latter does not have rigorous grounds, one could hardly estimate the accuracy of condition (15).

Meanwhile, one can point out a way which allows us to avoid the difficulties associated with the direct applicability of the superposition approximation. This way consists of the use of the well-known exact equation for the isothermal compressibility of the statistical system [12,28–30] at the preservation of the found physically correct form (16) for $B(r)$. For the crystal, this equation is as follows:

$$T\left(\frac{\partial n_0}{\partial p}\right)_T = 1 + \frac{n_0}{V}\int d\mathbf{r}\int d\mathbf{r}'[f(\mathbf{r},\mathbf{r}') - f(\mathbf{r})f(\mathbf{r}')] = 1 + n_0\int d\mathbf{R}[B(R)-1]\sum_{\mathbf{L}} f_{\mathbf{L}}^2 e^{ib_0\mathbf{L}\cdot\mathbf{R}}. \tag{17}$$

In the next sections, we will use just this equation [but not condition (15)] for the self-consistent determination of the parameter Y [which is a member of the function $B(r)$ from Eq. (16)].

III. THE SUM RULES AND SELF-CONSISTENT EQUATIONS

In what follows, it is convenient to transform Eq. (1) to the Fourier representation. Substituting form (5) for $f(\mathbf{r},\mathbf{r}')$ into Eq. (1), taking into account condition (11), and introducing the dimensionless parameter of the reciprocal lattice

$$\sigma = \frac{b_0 D}{2\sqrt{2}\pi}, \tag{18}$$

we come to the equation for the Fourier amplitudes,

$$T^{*}\mathbf{L}f_{\mathbf{L}} - \frac{1}{\pi^2}\sum_{\mathbf{L}'}\frac{\mathbf{L}'}{L'^3}f_{\mathbf{L}'}f_{\mathbf{L}-\mathbf{L}'}\hat{I}(\sigma L') = \mathbf{0}, \tag{19}$$

where

$$\hat{I}(\sigma L') = -i\frac{b_0{}^2 L'}{4\pi}\int d\mathbf{R}B(R)\frac{\mathbf{L}'\cdot\mathbf{R}}{R}\frac{d\hat{W}(R)}{dR}e^{ib_0\mathbf{L}'\cdot\mathbf{R}} = \int_0^{\infty} d\xi B(\xi)\frac{d\hat{W}(\xi)}{d\xi}[\sin(2\sqrt{2}\pi\sigma L'\xi) - 2\sqrt{2}\pi\sigma L'\xi\cos(2\sqrt{2}\pi\sigma L'\xi)], \quad L' \equiv |\mathbf{L}'|. \tag{20}$$

Here and below we use the designations $B(\xi)$ and $\hat{W}(\xi)$, where $\xi = R/D$, equally with $B(R)$ and $\hat{W}(R)$.

Nonlinear Eq. (19) at $\mathbf{L} \neq \mathbf{0}$ has either trivial (corresponding to a fluid) or, generally speaking, nonzero solutions $f_{\mathbf{L}}$ describing a crystal state of the system. To choose an appropriate construction of the nontrivial solutions, it is useful to determine their functional form at $L \to \infty$. To make this, let us use the Taylor expansion $f_{\mathbf{L}-\mathbf{L}'} = f_{\mathbf{L}} - L_i'(\partial f_{\mathbf{L}}/\partial L_i) + \cdots$ under the sum in Eq. (19). For the fcc crystal, the sums containing the products of odd numbers of the vector $\mathbf{L}'$ components in Eq. (19) reduce to zero, and in the first nonvanishing order on the derivatives we obtain the differential equation

$$f_{\mathbf{L}} + \frac{1}{\beta_{\infty}}\frac{df_{\mathbf{L}}}{d(L^2)} = 0, \tag{21}$$

where the self-consistent quantity $1/\beta_{\infty}$ is defined as

$$\frac{1}{\beta_{\infty}} = \frac{2}{3\pi^2 T^{*}}\sum_{\mathbf{L}'}\frac{1}{L'}f_{\mathbf{L}'}\hat{I}(\sigma L'). \tag{22}$$

The solution of Eq. (21) at $L \to \infty$,

$$f_{\mathbf{L}} \propto \exp(-\beta_{\infty}L^2), \tag{23}$$

has the physical meaning at $\beta_{\infty} \geqslant 0$ only; the series in Eq. (22) converges, obviously, at finite T^{*}.

From Eq. (19) follows the infinite number of exact sum rules facilitating a regular procedure of determination of the nontrivial solutions $f_{\mathbf{L}}$. To derive these rules, note that the term with $\mathbf{L}' = \mathbf{0}$ disappears identically from the sum in Eq. (19), which by itself turns into the identity at $\mathbf{L} = \mathbf{0}$. Considering $f_{\mathbf{L}}$, $f_{\mathbf{L}-\mathbf{L}'}$ as the continuous functions of their arguments, assuming $\mathbf{L}$ as the vector with arbitrary small but finite length L, and employing now the Taylor expansion of these functions on the vector $\mathbf{L}$ components, one can present the left-hand side of Eq. (19) as the series on the powers of L^2 beginning with the first one. Then, equating to zero the coefficients at each power of L^2, we can obtain any number of exact sum rules for this equation. Let us write out the first and the second of them,

$$T^{*} + \frac{2}{3\pi^2}\sum_{\mathbf{L}'}\frac{1}{L'}f_{\mathbf{L}'}\frac{df_{\mathbf{L}'}}{d(L'^2)}\hat{I}(\sigma L') = 0, \tag{24}$$

$$T^{*}\left.\frac{df_{\mathbf{L}}}{d(L^2)}\right|_{\mathbf{L}=0} + \frac{2}{3\pi^2}\sum_{\mathbf{L}'}\frac{1}{L'}f_{\mathbf{L}'}\left[\frac{d^2 f_{\mathbf{L}'}}{d(L'^2)^2} + \frac{2}{5}L'^2\frac{d^3 f_{\mathbf{L}'}}{d(L'^2)^3}\right]\hat{I}(\sigma L') = 0. \tag{25}$$

Asymptotic behavior (23) suggests the choice of the approximate solution of Eq. (19) at arbitrary $\mathbf{L}$'s. So, in the simplest approximation it is naturally to set

$$f_{\mathbf{L}} = \exp(-\beta L^2), \tag{26}$$

where the positive parameter β is subject to determination [at $L=0$, function (26), as it should, reduces to unity]. In this case, according to Eq. (12),

$$f(\mathbf{r}) = \sum_{\mathbf{L}} e^{-\beta L^2 + ib_0\mathbf{L}\cdot\mathbf{r}}. \tag{27}$$

It is important to note that the parameter β is closely connected with the thermal excitations, either oscillatory or responsible for the defect structure of the crystal. The present theory, being extremely nonlinear, does not need the special introduction of such model characteristics of the defect as the activation energy, etc. In the framework of the classical statistics at $T=0$, i.e., in the absence of lattice vibrations and crystal defects, it is obvious that $\beta=0$ and Eq. (27) is reduced to Eq. (4). Substituting Eq. (27) into the first sum rule (24), we find the self-consistent equation for the determination of the parameter β,

$$T^{*} - \frac{2\beta}{3\pi^2}\sum_{\mathbf{L}\neq 0}\frac{1}{L}e^{-2\beta L^2}\hat{I}(\sigma L) = 0. \tag{28}$$

The sum over the reciprocal-lattice vectors in Eq. (28) converges rather well at not too small β. However, as will be shown below, $\beta \approx 0.1$ even at $T^{*} \sim 1$ (note that the dimensionless temperature of the triple point for argon is ≈ 0.7 [24]). This means that for the description of the sublimation phenomenon of the noble-gas crystals, it is appropriate to transform Eq. (28) to a form containing a fast-convergent sum at $\beta \to 0$ over the direct lattice vectors $\mathbf{a}$. Such a procedure is based on the equality known as the theta-function transformation [34] and in application to Eq. (27) this equality gives

$$f(\mathbf{r}) = 2\left(\frac{\pi}{\beta}\right)^{3/2}\sum_{\mathbf{a}} e^{-(\mathbf{r}-\mathbf{a})^2 b_0{}^2/(4\beta)}. \tag{29}$$

Representation (29) is often used at the investigation of the freezing problem (see, for example, [13,18,35]).

Using Eq. (29) instead of Eq. (27), taking into account Eq. (20), and passing to the dimensionless vectors $\hat{\mathbf{h}}=\sigma\mathbf{a}/D$ of the fcc lattice, we can transform Eq. (28) to the following form:

$$T^* - \frac{8\pi^{5/2}\sigma^3}{3\beta^{3/2}}\int_0^\infty d\xi\xi^3\frac{d\hat{W}(\xi)}{d\xi}B(\xi)e^{-\pi^2\sigma^2\xi^2/\beta} - \frac{\sqrt{\beta}}{3\pi^{3/2}}\sum_{\hat{\mathbf{h}}\neq 0}\frac{1}{\hat{h}}\int_{-\infty}^{\infty} d\xi\frac{d\hat{W}(\xi)}{d\xi}B(\xi)\left[1-\frac{2\pi^2}{\beta}\sigma\xi(\hat{h}-\sigma\xi)\right]e^{-\pi^2(\hat{h}-\sigma\xi)^2/\beta} = 0. \tag{30}$$

Here, we used the formal invariance of $\hat{W}(\xi)$ and $B(\xi)$ with respect to the change $\xi \to -\xi$.

Performing the analogous procedure of transformation to Eqs. (17) and (13) and introducing the dimensionless density $n_0^* = n_0 D^3 = \sqrt{2}\sigma^3$ and pressure $p^* = pD^3/w_0$, we get

$$T^*\left(\frac{\partial n_0^*}{\partial p^*}\right)_{T^*} - \frac{4\pi^{5/2}\sigma^3}{\beta^{3/2}}\int_0^\infty d\xi\xi^2 B(\xi)e^{-\pi^2\sigma^2\xi^2/\beta} - \sqrt{\frac{\pi}{\beta}}\sigma^2\sum_{\hat{\mathbf{h}}\neq 0}\frac{1}{\hat{h}}\int_{-\infty}^{\infty} d\xi\xi[B(\xi)-1]e^{-\pi^2(\hat{h}-\sigma\xi)^2/\beta} = 0, \tag{31}$$

$$p^* = \sqrt{2}\sigma^3 T^* - \frac{8\sqrt{2}\pi^{5/2}\sigma^6}{3\beta^{3/2}} \times \int_0^\infty d\xi\xi^3\frac{d\hat{W}(\xi)}{d\xi}B(\xi)e^{-\pi^2\sigma^2\xi^2/\beta} - \frac{2\sqrt{2\pi}\sigma^5}{3\sqrt{\beta}}\sum_{\hat{\mathbf{h}}\neq 0}\frac{1}{\hat{h}}\int_{-\infty}^{\infty} d\xi\xi^2\frac{d\hat{W}(\xi)}{d\xi}B(\xi)e^{-\pi^2(\hat{h}-\sigma\xi)^2/\beta}. \tag{32}$$

In what follows, the well-known expression (see, for example, [12,27–30]) for the energy ϵ per atom of the crystal will be used. Being transformed with the help of the procedure applied above, the expression for the dimensionless energy $\epsilon^* \equiv \epsilon/w_0$ becomes as follows:

$$\epsilon^* = \frac{3}{2}T^* + \frac{8\pi^{5/2}\sigma^3}{\beta^{3/2}}\int_0^\infty d\xi\xi^2\hat{W}(\xi)B(\xi)e^{-\pi^2\sigma^2\xi^2/\beta} + 2\sqrt{\frac{\pi}{\beta}}\sigma^2\sum_{\hat{\mathbf{h}}\neq 0}\frac{1}{\hat{h}}\int_{-\infty}^{\infty} d\xi\xi\hat{W}(\xi)B(\xi)e^{-\pi^2(\hat{h}-\sigma\xi)^2/\beta}. \tag{33}$$

Equations (30)–(32) [simultaneously with Eqs. (3) and (16)] represent the closed system from which one can establish a single-valued parametric connection (by means of the parameters β and Y) between p^*, T^*, and the lattice constant $a_0=\sqrt{2}D/\sigma$ of the crystal. This connection leads to an equation of state which for given p^* will describe a real crystal phase at temperatures lower than the freezing temperature (depending on p^*). In the case of the crystal-gas transition, the dimensionless pressures at the sublimation line are small (even in the triple point of argon $p^* \sim 10^{-3}$ [26]). This fact noticeably simplifies the procedure of determination of the lattice constant and other thermodynamic functions near the sublimation line (see below).

IV. THE THEORY IN THE LOW-TEMPERATURE LIMIT

The found solution (16), taking into account Eq. (3), possesses a relevant behavior at $T^* \to 0$. In this case, all $f_{\mathbf{L}}=1$, $Y|_{T^*\to 0} \to 1-0$ (below we will show this rigorously), and $B(R)|_{T^*\to 0} \to \Theta(R-D)$ [i.e., $D'=D$ in Eq. (8)]. As a result, Eq. (17) with $f(\mathbf{r})$ from Eq. (4) turns into an identity.

It is useful to consider Eq. (32) at low temperatures by the scheme stated in Appendix A. Choosing the function $\xi^2 d\hat{W}(\xi)/d\xi$ as $G(\xi)$ in Eq. (A1) and acting as when calculating Eq. (A2), we obtain

$$p^* = \sqrt{2}\sigma^3 T^* - 4\sqrt{2}\sigma^9\left[A_6 - 2\sigma^6 A_{12} + \frac{3\beta}{2\pi^2}(5A_8 - 44\sigma^6 A_{14})\right], \tag{34}$$

where the known [31,32] fcc lattice sums A_n are defined by Eq. (A3). Then from Eq. (34) at $T^*=0$ (when $\beta=0$, see below) for the free crystal ($p^*=0$), it follows that

$$\sigma^{(0)} \equiv \sigma|_{T^*=0} = \left(\frac{A_6}{2A_{12}}\right)^{1/6} = 0.9173. \tag{35}$$

From Eq. (30), one can determine the explicit temperature dependence of β at $T^* \to 0$. Again, applying the scheme developed in Appendix A, we transform Eq. (30) to within the main terms to the form

$$T^* - \frac{2\beta\sigma^6}{\pi^2}(22\sigma^6 A_{14} - 5A_8) = 0. \tag{36}$$

Now, changing σ in Eq. (36) by $\sigma^{(0)}$ from Eq. (35), we find the following expression for the parameter β at $T^* \to 0$:

$$\beta = \frac{\pi^2 A_{12}^2 T^*}{A_6(11A_6A_{14} - 5A_8A_{12})} = 0.088\,11T^*. \tag{37}$$

It is important to note that solution (29) [as well as Eq. (27)] for the singlet function together with expression (37) for β turn out to be exact at $T^* \to 0$ in the framework of the classical statistics. This statement follows directly from the fact that the low-temperature value of the heat capacity in our theory (see Appendix A) is determined by the classical Dulong and Petit law [32,33].

However, these results are based on the assumption about the overlinear character of the temperature dependence of Y at $T^* \to 0$. The explicit expression for Y, derived in Appendix B and applicable at low temperatures, confirms this assumption. Substituting the numerical values of the lattice sums A_n (see Appendix A) into Eq. (B3), we obtain

$$Y|_{T^* \to 0} = 1 - 7.942 \times 10^{-4} T^{*3/2}. \tag{38}$$

Thus, due to obtained dependence (38), one can really put $B(\xi) = \Theta(\xi - 1)$ when calculating the contributions linear on T^* into Eqs. (30)–(33). Pay attention to the smallness $(\sim 10^{-3})$ of the numerical factor in expression (38).

Besides, the theory allows us to calculate the coefficient of thermal expansion α of the Lennard-Jones crystal in the limit $T^* \to 0$. Although the result of the calculation does not follow the Nernst theorem (because the nonquantum approach is used [33]), it seems rather instructive.

We will base the calculation on expression (34). Now, the zero-temperature value $\sigma^{(0)}$ from Eq. (35) should be substituted into the terms $\sim T^*$ and $\sim \beta$ in Eq. (34). Other terms on the right-hand side of Eq. (34) should be expanded up to the first nonvanishing term $\sim \delta\sigma/\sigma^{(0)} \equiv (\sigma - \sigma^{(0)})/\sigma^{(0)}$. Because we are interested in the thermal expansion of the free crystal, the pressure given by Eq. (34) must be equal to the pressure of the saturated vapor being in the thermodynamic equilibrium with the crystal. But the vapor pressure at $T^* \to 0$ behaves according to the Clapeyron-Clausius equation [33], i.e., as $\sim \exp(-8.607/T^*)$ (see the next section). So, at $T^* \to 0$ one can neglect this exponentially low vapor pressure and write the equilibrium condition for the crystal in the form

$$p^* = \sqrt{\frac{A_6}{A_{12}}} T^* \left(1 + 3\frac{22A_6A_{14} - 5A_8A_{12}}{11A_6A_{14} - 5A_8A_{12}}\right) + 12A_6\left(\frac{A_6}{A_{12}}\right)^{3/2} \frac{\delta\sigma}{\sigma^{(0)}} = 0. \tag{39}$$

Proceeding to the relative change of the lattice constant $\delta a_0/a_0^{(0)} = -\delta\sigma/\sigma^{(0)}$ $(a_0^{(0)} \equiv \sqrt{2}D/\sigma^{(0)})$, we find from Eq. (39) the low-temperature value of the linear coefficient of thermal expansion of the crystal,

$$\alpha^{(0)} = \frac{1}{a_0} \left.\frac{\partial a_0}{\partial T}\right|_{T \to 0} = \frac{A_{12}}{12 w_0 A_6^2} \frac{77A_6A_{14} - 20A_8A_{12}}{11A_6A_{14} - 5A_8A_{12}}. \tag{40}$$

From here, for argon ($w_0 = 121$ K [31,32]), we obtain $\alpha^{(0)} = 3.62 \times 10^{-4}\ \mathrm{K}^{-1}$.

The found $\alpha^{(0)}$ is approximately half of the α value measured experimentally at the triple-point temperature of argon [24]. In Sec. VI, we will show that our theory leads to a noticeable growth of α of the Lennard-Jones crystal with the temperature.

V. THE EQUILIBRIUM SUBLIMATION OF THE LENNARD-JONES CRYSTALS

To find the sublimation line on the phase diagram of the noble-gas medium, it is necessary to add to Eqs. (30)–(32) the conditions expressing the equality of the chemical potentials of the crystal and its saturated vapor at one and the same pressure of the coexisting phases. The problem is simplified due to the fact that the vapor phase can be described with good accuracy in the ideal gas approximation. However, one encounters the following complication. Unlike p and ϵ, the entropy per particle s as well as the chemical potential [33]

$$\mu = \epsilon - Ts + \frac{p}{n_0} \tag{41}$$

are formally expressed through the whole of the correlation functions of the medium [28,29]. In other words, s can be written in the form (see, for example, [28])

$$\begin{aligned} s = 5/2 &+ \ln\left[\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\frac{1}{n_0}\right] + \frac{1}{TV}\int d\mathbf{r}\,\Psi_1(\mathbf{r})f(\mathbf{r}) \\ &+ \frac{n_0}{2TV}\int d\mathbf{r}\int d\mathbf{r}'\,\Psi_2(\mathbf{r},\mathbf{r}')f(\mathbf{r},\mathbf{r}') \\ &+ \frac{n_0^2}{6TV}\int d\mathbf{r}\int d\mathbf{r}'\int d\mathbf{r}''\,\Psi_3(\mathbf{r},\mathbf{r}',\mathbf{r}'')f(\mathbf{r},\mathbf{r}',\mathbf{r}'') + \cdots . \end{aligned} \tag{42}$$

Here, "the ideal gas" part of the entropy [33] (with m as the atomic mass) is represented explicitly and the so-called correlation potentials of the groups of particles are introduced,

$$\Psi_1(\mathbf{r}) = -T\ln f(\mathbf{r}), \quad \Psi_2(\mathbf{r},\mathbf{r}') = -T\ln\left[\frac{f(\mathbf{r},\mathbf{r}')}{f(\mathbf{r})f(\mathbf{r}')}\right],$$
$$\Psi_3(\mathbf{r},\mathbf{r}',\mathbf{r}'') = -T\ln\left[\frac{f(\mathbf{r},\mathbf{r}',\mathbf{r}'')f(\mathbf{r})f(\mathbf{r}')f(\mathbf{r}'')}{f(\mathbf{r},\mathbf{r}')f(\mathbf{r},\mathbf{r}'')f(\mathbf{r}',\mathbf{r}'')}\right], \ldots . \tag{43}$$

Nevertheless, the problem of interest can be resolved quantitatively. In fact, in Kirkwood's approximation (6) we have $\Psi_3(\mathbf{r},\mathbf{r}',\mathbf{r}'') \equiv 0$ and so the next (after the two-particle) nonzero contribution into the entropy will correspond to the four-particle correlations. But taking into account the latter ones oversteps the limits of the accepted approximation based on the equations for the singlet and pair correlation functions. So, we can restrict ourselves to the next form of the entropy of the crystal phase,

$$\begin{aligned} s = \tfrac{5}{2} &+ \ln\left[\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\frac{1}{n_0}\right] - \frac{1}{V}\int d\mathbf{r}\,f(\mathbf{r})\ln f(\mathbf{r}) \\ &- \frac{n_0}{2V}\int d\mathbf{r}\int d\mathbf{r}'\,f(\mathbf{r})f(\mathbf{r}') \times B(|\mathbf{r}-\mathbf{r}'|)\ln B(|\mathbf{r}-\mathbf{r}'|). \end{aligned} \tag{44}$$

Pay attention to the fact that the structure of Eq. (44) resembles somewhat the form of the thermodynamic potential used in the density-functional theory of freezing [13]. Note, however, that in the present approach either the singlet or the pair correlation functions of the crystal are determined self-consistently, without the use of any excess information about the two-body direct correlation function of the corresponding liquid.

Let us turn our attention to the first integral term on the right-hand side of Eq. (44). Using representation (29), which at $\beta \ll 1$ is the sum of the δ-like functions, one can replace the integral by the sum of N equal integrals, constructed with the help of any of these functions ($N = n_0 V$ is the whole number of the nodes in the volume V). In view of the fast convergence of the integrals, one can extend the integration on the whole space. Then, bearing in mind Eq. (11), we obtain at $\beta \ll 1$

$$\frac{1}{V}\int d\mathbf{r} f(\mathbf{r}) \ln f(\mathbf{r}) = \ln\left[2\left(\frac{\pi}{e\beta}\right)^{3/2}\right]. \qquad (45)$$

As to the last term on the right-hand side of Eq. (44), it can then be reduced to the form

$$-\frac{2\pi^{5/2}\sigma^3}{\beta^{3/2}}\int_0^\infty d\xi \xi^2 B(\xi)\ln[B(\xi)] e^{-\pi^2\sigma^2\xi^2/\beta}$$
$$-\sqrt{\frac{\pi}{\beta}}\frac{\sigma^2}{2}\sum_{\hat{\mathbf{h}}\neq 0}\frac{1}{\hat{h}}\int_{-\infty}^{\infty} d\xi \xi B(\xi)\ln[B(\xi)] e^{-\pi^2(\hat{h}-\sigma\xi)^2/\beta}. \qquad (46)$$

At $\beta \ll 1$, the function $B(\xi)$ in the integrands under the sum is close to unity in the essential domain of integration. So, one can replace $B(\xi)\ln[B(\xi)]$ by $B(\xi)-1$. After that, comparing with Eq. (31) and using the results of Appendix B, we estimate Eq. (46) as $\approx -T^* A_{12}/(8A_6^2) \propto -0.01T^*$.

Now, substituting Eq. (45) into Eq. (44) and neglecting Eq. (46), we can write the condition $\mu = \mu_G$ (the quantities relating to the gas phase are characterized by the subscript "G") using the known [33] expressions for the thermodynamic functions of the ideal gas. Then, neglecting p/n_0 in comparison with p/n_{0G} we find the following equation in the dimensionless units:

$$\ln p^* = \frac{\epsilon^*}{T^*} - 4 + \ln\left[\left(\frac{2\pi}{\beta}\right)^{3/2}\sigma^3 T^*\right], \qquad (47)$$

where ϵ^* is determined by Eq. (33).

Equation (47) (together with the equations obtained in Sec. III) determines the theoretical sublimation line on the phase diagram of the Lennard-Jones medium.

VI. THE NUMERICAL CALCULATION SCHEME AND RESULTS

To calculate the thermodynamic characteristics of the Lennard-Jones crystal in the "classical" domain of temperatures, we have undertaken the numerical solution of Eqs. (30)–(32). The strategy of the calculations is as follows. Let us fix some temperature and find the values β, σ, and Y as the solutions of Eqs. (30) and (31), and the requirement that the sublimation pressure (32) must be close to zero [26]. Keeping in mind the calculation of the isothermal compressibility of the crystal in the vicinity of the sublimation line, we will search two sets of solutions: σ_1, β_1, Y_1 and σ_2, β_2, Y_2 at somewhat distinguishing p^*'s for each temperature.

Finding the parameters β, σ, and Y, we, in principle, can obtain p^* either positive or negative. Although the negativeness of the pressure is the feature of a metastable state [33], in itself the possibility of the description of such states by the theory undoubtedly demonstrates its completeness. It is important, however, that for any equilibrium physical situation, the pressure, of course, will be positive [see Eq. (47)].

The low-temperature analytical expressions obtained in Sec. IV are suitable at $T^* \neq 0$ as the zero approximations for the corresponding numerical solutions of Eqs. (30)–(32). The numerical analysis of these equations has been realized by the use of the computer package MATHEMATICA 4.2. The values of the terms with $1 \leqslant \hat{h} \leqslant 7\sqrt{2}$ in the lattice sums were found by direct numerical calculation taking into account the fcc symmetry. The residues of the sums were replaced by the corresponding integrals in the $\hat{\mathbf{h}}$ space by analogy with what has been made when transferring to Eq. (B2). In this case, rather high accuracy of the calculations was achieved. The numerical procedure was considered as realized when the absolute values of the left-hand sides of Eqs. (30) and (31) were found to be less than 10^{-6}.

We should address separately the calculations by Eq. (31), which, in fact, represents by itself the differential relation between the thermodynamic quantities. It is essential, however, that we know the exact (in the framework of the classical statistics) value of the isothermal compressibility of the Lennard-Jones crystal at $T^* = 0$. Using this value as the zero approximation in Eq. (31) at some given low temperature, for example at $T^* = 0.25$, we will carry out the numerical calculations of σ_1, β_1, Y_1 and σ_2, β_2, Y_2. From here, we will find a new (corresponding to the first approximation) value of the isothermal compressibility at $T^* = 0.25$. After that, we will fulfill the calculation with this new value of the compressibility and, using the results of the calculation, we will find the isothermal compressibility in the second approximation. By comparison with the calculations of the first approximation, we will make sure there is good convergence of the numerical procedure used.

Then, we choose the following value: $T^* = 0.35$. Substituting into Eq. (31) as the zero approximation the value of the isothermal compressibility found in the second approximation at the previous, $T^* = 0.25$, temperature, we will repeat the above described procedure of finding the sets of solutions and the isothermal compressibility at $T^* = 0.35$.

In this way, we have calculated the pointed out values at $T^* = 0.25$, 0.35, 0.45, 0.55, 0.65, and 0.6875 (the last value, being multiplied by $w_0 = 121$ K [31,32], corresponds to the temperature 83.2 K of the triple point of argon [24]). In addition, the formal calculations have been performed also at the temperature $T^* = 0.75$, which exceeds the triple-point temperature of the Lennard-Jones media. The isothermal compressibility

$$\chi_T = \frac{1}{n_0}\left(\frac{\partial n_0}{\partial p}\right)_T = \frac{D^3}{w_0}\frac{1}{n_0^*}\left(\frac{\partial n_0^*}{\partial p^*}\right)_{T^*} = 3\frac{D^3}{w_0}\frac{1}{\sigma}\left(\frac{\partial \sigma}{\partial p^*}\right)_{T^*} \qquad (48)$$

has been found from the results of the numerical calculations by means of the replacement of the derivative by the ratio of

TABLE I. The numerical values of the parameters of the distribution functions, together with the thermodynamic values of the Lennard-Jones crystal in the vicinity of the sublimation line (the first approximation).

T^*	0.25	0.35	0.45	0.55	0.65	0.6875	0.75
σ_1	0.9049	0.9012	0.8969	0.8919	0.887	0.8851	0.8815
$10^2\beta_1$	2.335	3.283	4.283	5.373	6.529	7.005	7.832
$10^3(1-Y_1)$	0.187	0.376	0.603	1.018	1.719	2.13	2.694
$10^2p_1^*$	0.05575	0.8624	5.063	0.4857	0.4941	0.6986	0.7613
σ_2	0.9047	0.9011	0.8965	0.8918	0.887	0.8849	0.8813
$10^2\beta_2$	2.341	3.287	4.302	5.385	6.536	7.017	7.851
$10^3(1-Y_2)$	0.188	0.377	0.604	1.019	1.72	2.132	2.698
$10^2p_2^*$	−3.412	−0.664	−0.1029	−1.633	−0.5189	−0.9181	−1.314
$10^2(\partial n_0^*/\partial p^*)_{T^*}$	1.874	2.031	2.173	2.501	2.735	2.854	3.082

the finite differences $[(\sigma_1-\sigma_2)/(p_1^*-p_2^*)]_{T^*}$ (with $1/\sigma$ being intermediate between $1/\sigma_1$ and $1/\sigma_2$ at each temperature).

The numerical calculation of the parameters according to the above-described scheme led in the first approximation to the results shown in Table I.

Remember that at $T^*=0$ for the free crystal (when $Y=1$, $p^*=0$) we have $\sigma^{(0)}$ from Eq. (35) and $(\partial n_0^*/\partial p^*)_{T^*=0} = A_{12}/(4A_6^2)=0.014\,52$.

To illustrate the above-mentioned statement about the good convergence of the numerical procedure, we give in Table II the parameter values calculated in the second approximation at $T^*=0.75$ [compare the values of $(\partial n_0^*/\partial p^*)_{T^*}$ in Tables I and II].

VII. DISCUSSION OF THE RESULTS

In Fig. 1, the experimental (collected in Ref. [24]) values of the lattice constant a_0 of argon at the saturated vapor pressures are given. Crosses show the theoretical (see Table I) values of $a_0=\sqrt{2}D/\sigma$, where $D=3.40$ Å for argon [31,32] (with σ situated between σ_1 and σ_2 at each temperature). The calculated values of a_0 are connected by a smooth curve in the temperature domain where the experimental data are well described by the theory based on the classical statistics. In addition, the dashed line in Fig. 1 shows the hypothetical (in the zero approximation) temperature dependence of a_0 if one should use the zero-temperature value $\alpha^{(0)}=3.62\times10^{-4}$ K^{-1} [see Eq. (40)] in the whole temperature range.

The quantitative closeness between the theory and experimental data at $T\geqslant30$ K, or $T^*\geqslant0.25$ (Fig. 1), means, in fact, that the domain of applicability of the proposed classical approach begins from $T^*\approx0.25$. It is interesting to note that the temperature at which a_0 comes to the classical behavior is consistent with the results of the Debye model [33] predicting the classical behavior of the specific heat of the solid at $T\geqslant\Theta_D/4$, where Θ_D is the Debye temperature of the crystal; $\Theta_D=85$ K for argon [32].

Numerically, the difference between the calculated and measured temperature dependencies of a_0 for argon even near the triple point does not exceed 0.5% (Fig. 1). It is useful to note that the difference between the dashed line and the experimental data near the triple point (Fig. 1) is ≈1%.

In Fig. 2, the experimental (according to the data collected in Ref. [22]) values of the isothermal compressibility of the crystal argon at the saturated vapor pressure are presented. The results of calculation according to the theory [see Eq. (48) and Table I] are represented by the crosses and are connected by the smooth curve. Again, as in Fig. 1, one can see good quantitative agreement between the theory and experiment at temperatures above 30 K. But when approaching the triple point, the theoretical results are found to be underestimated in comparison with the experimental data (notice, however, the rather large-scale scatter of the experimental χ_T values reported by different authors).

Finally, in Fig. 3 the experimental (from [26]) points determining the dimensionless sublimation lines of three classical noble-gas crystals are collected. The crosses show the theoretical [with formulas (47) and (33) taking into account the data of Table I] values of p^*. The curve, which rather well approximates the theoretical points, is described by the equation

$$\ln p^* = \lambda^* - \frac{q^*}{T^*} \qquad (49)$$

with $\lambda^*=4.527$ and $q^*=8.104$. Note that the curve fitting the experimental data in Fig. 3 in the best (by the method of least squares) manner is presented in [26] in the form of Eq. (49) with $\lambda^*=5.302$ and $q^*=8.206$. Pay attention to the proximity of the theoretical and experimental q^* values in the discussed

TABLE II. The same as Table I in the second approximation ($T^*=0.75$).

σ_1	$10^2\beta_1$	$10^3(1-Y_1)$	$10^2p_1^*$	σ_2	$10^2\beta_2$	$10^3(1-Y_2)$	$10^2p_2^*$	$10^2(\partial n_0^*/\partial p^*)_{T^*}$
0.8816	7.836	2.932	1.79	0.8813	7.873	2.94	−2.209	3.083

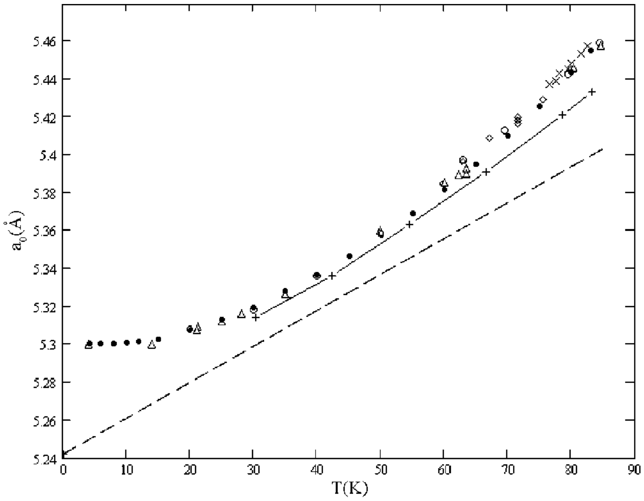

FIG. 1. The temperature dependence of the lattice constant of argon at the saturated vapor pressure. Solid circles (●) denote the experimental data of [24]; ○, ×, ◇, △ indicate the data of other authors shown in [24]. The results of calculations according to our theory are denoted by + and connected by a smooth curve in the region of applicability of the classical statistics. The dashed straight line corresponds to the theoretical calculation in the zero approximation [see Eq. (40)].

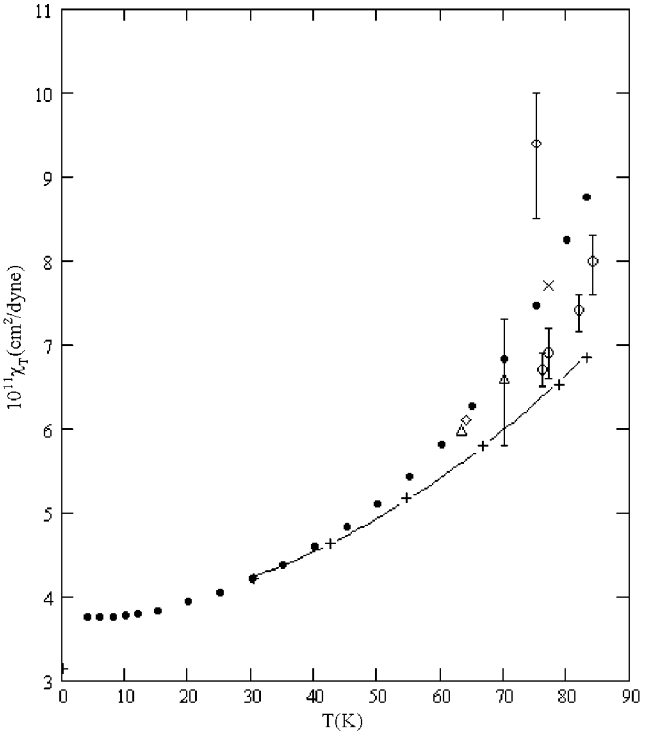

FIG. 2. The isothermal compressibility of crystal argon vs temperature. Solid circles (●) represent the experimental data of [24]; ○ indicate the data of [22]; ×, ◇, △ indicate the data of other authors shown in [22]. The results of calculations according to our theory are denoted by + and connected by a smooth curve in the region of applicability of the classical statistics.

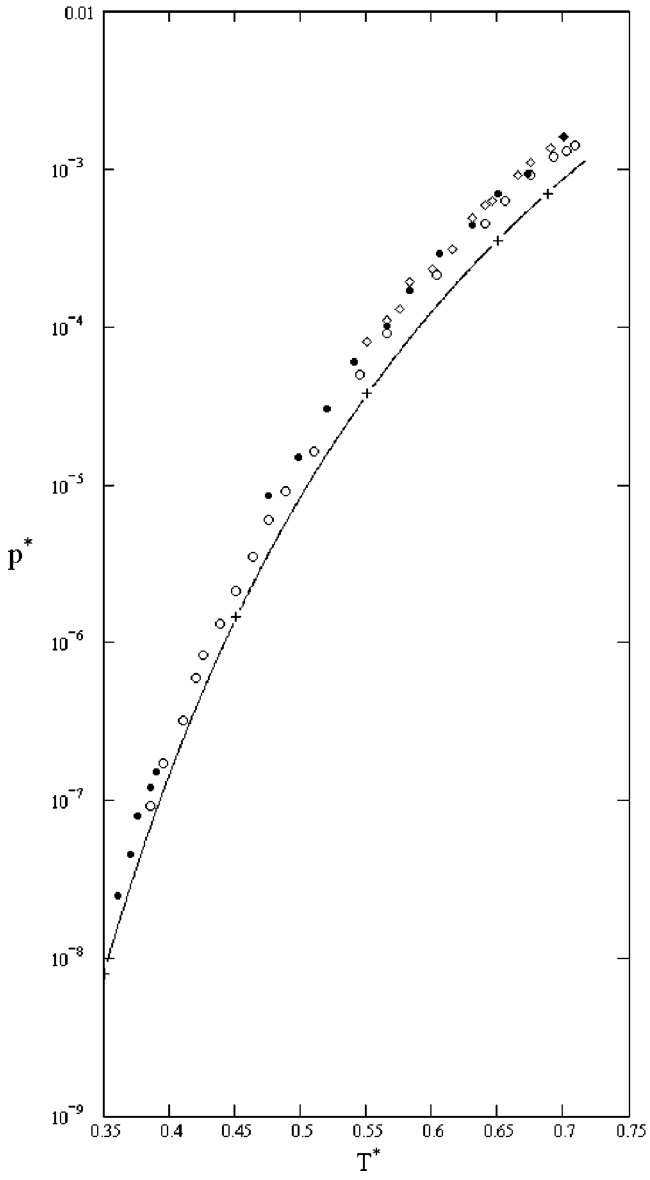

FIG. 3. The experimental (according to [26]) dependencies of the sublimation pressure vs temperature (in the reduced units) for Ar (◇), Kr (○), and Xe (●). The results of calculations according to our theory are denoted by + and connected by the curve [represented by Eq. (49) with the parameter values given in the text].

temperature domain [at $T^*=0$, the dimensionless heat of sublimation of the Lennard-Jones crystal coincides with $-\epsilon^*|_{T^*=0}=A_6^2/(2A_{12})=8.607$; see Eqs. (A4) and (35)].

Figure 3 is of particular interest. The fact that the theoretical (in the dimensionless units) sublimation line passes close enough to the experimental points for the "classical" noble-gas media may mean that the terms taken into account in the expression for the solid-state entropy are, really, much more essential than the rejected ones. Thus, the general arguments of the theory get the additive confirmation.

As to the observed disagreement between the theory and the experimental data in Figs. 1–3, at low temperatures it is conditioned, as has been already mentioned, by the quantum effects. The conventional quantum theory of solids is well-developed in the harmonic approximation [32,36,37], but it cannot be used, in principle, for the purposes of the present paper (in order to describe, for example, the thermal expansion of the crystal). On the other hand, the anharmonic phonon theory (see, for example, [37]) operating with many-phonon processes (usually with three- and four-phonon ones) meets the well-known difficulties, the first of which is computational. So, the construction of a quantum analog of the theory proposed in the present paper is the actual but not simple problem.

One more reason for the disagreement can be stipulated by the use of the pair Lennard-Jones potential with the "gas" values of the parameters [32]. For the condensed matter, the role of three-body forces could also be found to be important [12,32].

It is useful to note that the theoretical sublimation curve [Eq. (47)] can be formally continued beyond the triple point temperature (see Tables I and II). In this sense, the triple point is not a singular one for the thermodynamic functions. But to locate it, one must study the phase equilibrium between the crystal and the liquid. In light of the results presented in this paper, now we have the possibility (apparently for the first time) to approach the problem of melting from the positions of the consistent theory of the crystal state. Concerning the theory of liquids, at present one has a number of sufficiently valid approaches in this field ([4–7]; see also, for example, Refs. [38–40]). It gives us hope to achieve a consistent description of the phase equilibrium for the Lennard-Jones medium in the whole p^*-T^* plane.

Let us touch upon the question of the bifurcation line which separates the domain of possible existence from the domain of the absence, in principle, of the crystal solutions at the phase diagram of the Lennard-Jones system. In fact, the identification of the melting point with the bifurcation point was realized, beginning from Kirkwood and Monroe [8], by many authors (for example, [9–11]). In the communication [41] presented by the author at the International Conference on Theoretical Physics (TH-2002, Paris), the phenomenon of bifurcation was analyzed in connection with the freezing problem [however using condition (15), but not the strong relation (17)].

On the other hand, using some model form for the pair function and studying the equation for the singlet function of the statistical system, the authors of Ref. [21] came to the conclusion that the physical characteristics in the bifurcation point do not correspond to those taking place in real substances at melting.

In fact, this conclusion is consistent, qualitatively, with that following from the results of the present paper. In fact, because at a given temperature the crystal must become harder when the pressure increases, one can expect the bifurcation of the solution at lowering pressure. As one can see from Table I, the crystal solutions exist in the negative pressure domain as well (i.e., formally, when the crystal is under a uniform extension). This means that at the bifurcation line, the pressure will surely be negative, at least for $T^* < 0.75$. Thus, we arrive at the definite conclusion that the bifurcation points do not have a direct relation to the melting-freezing phenomenon for real systems, at least in the vicinity of the triple point of the noble-gas media.

Besides, using the calculation scheme described, one can make sure that Eqs. (30)–(32) have an additional branch of solutions. However, the bifurcation problem in this case turns out to be absolutely irrelevant, because the additional branch by itself demonstrates a nonphysical behavior which is inconsistent with the limiting form (4). To verify this, we take notice of the fact that in the limit $T^*=0$ (and $p^*=0$), Eq. (30), besides the physically correct solution (37), allows a nonzero solution for β. The latter, according to the numerical calculations, is found to be equal to 0.1797. In this case, for σ we obtained the value 0.9628, which contradicts the exact (in the framework of the classical statistics) result (35). Hence, we come to the conclusion that the additional branch does not have a physical meaning and must be rejected.

From here one more, albeit indirect, conclusion follows. As we have shown in this paper, the only singlet and pair functions leading to the exact results in the limit of the perfect crystal can provide a correct description of the crystal state, including the phenomena of sublimation and melting. So, any attempt to study the problem of freezing by modeling the pair function of the crystal with the help of one or another supposition (for example, starting from the pair function of the liquid) must be considered extremely carefully.

Finally, let us outline briefly the ways to further develop the theory. In the first place, from Figs. 1–3 one can see a tendency to deviate between theory and experiment. This may indicate that the simplest form (26), based on the first sum rule, is no longer enough to lead to the precision description of the "high-temperature" experiments. So, to make the theoretical results more precise, it is necessary to use the second sum rule. In the second place, an extension of the theory in the case of crystal-liquid equilibrium seems to be the most important continuation of the investigations started in this paper. In the third place, having in mind the low-temperature phenomena in the crystals, it would be desirable to develop a quantum-statistical analog of the theory given in the present paper.

VIII. CONCLUSIONS

Starting directly from the equations for the singlet and pair correlation functions of the classical statistical medium with pair (for example, by Lennard-Jones) interaction between atoms, for the first time we constructed a consistent (free of any fitting parameters) theory describing the thermodynamic properties of the noble-gas crystals. The equation for the singlet function is presented in a form demonstrating the existence of an infinite number of exact sum rules for the amplitudes of space-periodic solutions. It is shown that already the first of the rules leads to the solutions which reproduce the exact form of the singlet function in the crystal at absolute zero. For the pair function, we obtained the self-consistent, physically correct form depending on the parameter determined by the integrated statistical characteristics of the system. To make the theory completely closed, we used the known exact relation for the isothermal compressibility of the system. As a result, the equation of state of the crystal can be recovered. The theory allows us to obtain the analytical expressions for the fundamental thermodynamic characteristics of the crystal in the main approximation, whereas subsequent numerical calculations lead to more exact results.

These results agree rather well with the corresponding experimental data for argon in the temperature region where the classical statistics is applicable. Further, we obtained the expression for the crystal entropy in the main approximation and constructed the sublimation curve, which with satisfactory accuracy reproduces that measured experimentally for the classical noble-gas media. The analysis of the phenomenon of bifurcation of the found solutions showed that the bifurcation points are placed outside the domain of pressures and temperatures typical for the freezing of the real noble-gas media. Ways to further develop the theory are discussed.

ACKNOWLEDGMENTS

I express my deep gratitude to Professor J. Lebowitz for the discussion of the basic ideas of the paper at the Paris International Conference on Theoretical Physics (TH-2002). Separate thanks go to Dr. S. I. Kosenko for the assistance with some numerical calculations.

APPENDIX A

At $T^* \to 0$, the power-type terms on T^* in Eqs. (30)–(33) appear from the integrals containing the δ-like functions $\exp[-\pi^2(\hat{h}-\sigma\xi)^2/\beta]$ in the integrands with $\hat{\mathbf{h}} \neq \mathbf{0}$. To find such terms, let us use the following expansion at $\beta \to 0$:

$$\int_{-\infty}^{\infty} d\xi G(\xi) e^{-\pi^2\sigma^2(\xi-\hat{h}/\sigma)^2/\beta} = \frac{1}{\sigma}\sqrt{\frac{\beta}{\pi}}\left[G(\xi) + \frac{\beta}{4\pi^2\sigma^2}\frac{d^2G(\xi)}{d\xi^2} + \cdots\right]\Bigg|_{\xi=\hat{h}/\sigma}, \tag{A1}$$

where $G(\xi)$ is any function having no singularities at the points $\xi = \hat{h}/\sigma$.

The function $G(\xi) = \xi\hat{W}(\xi)B(\xi)$, which is present in the integrands of the terms under the sum (33), possesses such a property and also (taking into account the overlinear temperature dependence of Y) it is enough to put $B(\hat{h}/\sigma) = 1$. Then we have from Eq. (33) in the low-temperature limit

$$\epsilon^* = \tfrac{3}{2}T^* + 2\sigma^6(\sigma^6 A_{12} - A_6) + \frac{3\sigma^6\beta}{\pi^2}(22\sigma^6 A_{14} - 5A_8), \tag{A2}$$

where $A_6 = 14.45$, $A_8 = 12.80$, $A_{12} = 12.13$, and $A_{14} = 12.06$ are the known numerical values for the fcc lattice sums [31,32],

$$A_n = \sum_{\hat{\mathbf{h}}\neq 0} \frac{1}{\hat{h}^n}, \hat{h} \equiv |\hat{\mathbf{h}}|. \tag{A3}$$

At last, substituting $\sigma^{(0)}$ from Eq. (35) into the term $\sim\beta$ in Eq. (A2) and also taking into account Eq. (37), we obtain

$$\epsilon^* = 3T^* + 2\sigma^6(\sigma^6 A_{12} - A_6). \tag{A4}$$

As a result, we find from Eq. (A4) that the heat capacity per atom of the classical crystal at constant volume V (or, identically, at constant $\sigma = \sigma^{(0)}$) in the limit $T^* \to 0$ is equal to $(\partial\epsilon^*/\partial T^*)_\sigma|_{T^*=0} = 3$, which coincides with the classical Dulong-Petit value [32,33].

APPENDIX B

To find the temperature dependence of Y at $T^* \to 0$, we will start with Eq. (31). Then, obtaining Eqs. (34) and (36) and omitting terms inessential at $T^* \to 0$ [as when obtaining Eqs.(34) and (35)], we arrive at the equation

$$T^*\left(\frac{\partial n_0^*}{\partial p^*}\right)_{T^*} = (1-Y) \times \sum_{\hat{\mathbf{h}}\neq 0} \frac{1 - \exp[4\hat{W}(\hat{h}/\sigma)/T^*]}{Y + (1-Y)\exp[4\hat{W}(\hat{h}/\sigma)/T^*]}. \tag{B1}$$

The sum in Eq. (B1) diverges at $T^* \to 0$ because a vast domain of the lattice vectors with $\hat{h} \geqslant 1$ contributes to the sum. In this case, one can replace the sum by the integral keeping in mind that the Bravais cube of the fcc lattice contains four primary cells [33]. Besides, we can put $Y = 1$ in the terms under the sum (integral) in Eq. (B1). Then the latter turns into the following equation:

$$T^*\left(\frac{\partial n_0^*}{\partial p^*}\right)_{T^*} = (1-Y)4\frac{4\pi}{2^{3/2}} \times \int_1^{\infty} d\hat{h}\hat{h}^2[1 - e^{4\hat{W}(\hat{h}/\sigma)/T^*}]. \tag{B2}$$

In the limit $T^* \to 0$, as one can see, the expression in the square brackets in the integrand can be approximately replaced by unity at $(1/\sigma) < \xi < 2^{1/3}T^{*-1/6}$; at $2^{1/3}T^{*-1/6} < \xi < \infty$, one can expand the exponential retaining two leading terms of the expansion. After that, the right-hand side of Eq. (B2) up to the main terms becomes as follows: $16\sqrt{2}\pi\sigma^3(1-Y)/(3\sqrt{T^*})$. At last, finding the derivative $(\partial p^*/\partial n_0^*)_{T^*=0} = 4A_6^2/A_{12}$ with the help of Eqs. (34) and (35), we obtain

$$(1-Y)|_{T^*\to 0} = \frac{3A_{12}^{3/2}}{64\pi A_6^{5/2}} T^{*3/2}. \tag{B3}$$

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