THERMODYNAMIC PROPERTIES OF SIMPLE ANHARMONIC CRYSTALS

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The equation of state earlier suggested for simple molecular crystals in the high-temperature region is applied to the calculation of thermodynamic functions of solid argon, krypton, xenon, and radon.

An attempt is made in the present paper to apply a new statistical approach, making it possible to calculate thermodynamic properties of simple crystals at high temperatures and subject to strong anharmonic effects, to the solidified rare gases. The method of calculation is based on a perturbation theory earlier suggested by the present authors for classical one-component crystals [1]. The equation of state in the second approximation of this theory is

$$P = P_0 + \Theta \frac{\partial}{\partial v} \ln v_f + \Theta \frac{\partial}{\partial v} \overline{W}, \tag{1}$$

where

$$v_f = \int_v \exp\{-U_{1,0}/\Theta\}\, dv$$

is the so-called free volume, and

$$\overline{W} = (2v_f^2)^{-1} \sum_{j>1} \int_{v_1}\int_{v_j} (\exp\{-W_{ij}/\Theta\} - 1) \exp\{-[U_{1,0}(1) + U_{1,0}(j)]/\Theta\}\, dv_1 dv_j \tag{2}$$

is a second approximation correction, taking into account the correlation between displacements of particle pairs in the crystals.

The free energy and other thermodynamic functions are obtained from Eq. (1) by well-known thermodynamic relations. In this case we choose as reference the free energy of an ideal gas lattice [2]

$$A_{\text{id}}^{\text{lat}} = -\Theta \ln\{vh^{-3}(2\pi m\Theta)^{3/2}\}.$$

It was shown in [3] that in the first approximation the results are in good agreement with those of computer experiments performed by the Monte Carlo method for the pressure and internal energy at high temperatures. This comparison is an indirect verification of the fast convergence of the expansion method [1]. However, to study the convergence of the expansions used in [1] of particle distribution functions and of thermodynamic functions, it is necessary to perform calculations to a second-order approximation. Such a calculation was carried out in [4]. It makes it possible not only to address the convergence problem, but also to estimate the contribution of binary correlations to the equilibrium properties in the range of high temperatures and pressures.

TABLE 1. Correlation Correction $\overline{W}$ for a Lennard-Jones Crystal

T^*	$\rho^*=1{,}00$	1,05	1,10	1,15	1,20
Harmonic approximation	0,194	0,209	0,217	0,226	0,232
1,17	0,262	0,264	0,259	0,255	0,254
1,35	—	0,269	0,265	0,260	0,257
2,74	—	—	0,278	0,286	0,283

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TABLE 2. Potential Parameters of Rare Gas Molecules Used in Present Calculation

Gas	σ, A	ε/k, K
Argon	3,400	119,0
Krypton	3,638	164,44
Xenon	3,961	231,08
Radon	4,27	290

In the second approximation the equilibrium properties of the crystal are determined by the magnitude of the correlation correction $\bar{W}$. The problem consists of calculating the sixth-dimensional integral of Eq. (2). An analytic expression was derived in [4] for the correlation correction in the harmonic approximation. In this approximation the quantity $\bar{W}$ depends on the derivative values of the Lennard-Jones potential at the lattice sites, i.e., it is a function of density only, but not of temperature. This makes it possible to estimate the contribution of pair correlations to the pressure and entropy values. To estimate the second-approximation contribution of the method used to the internal energy and heat capacity, it is necessary to take into account anharmonic effects in calculating the correlation corrections (2). In the low-temperature region one can confine the calculation to third- and fourth-order terms in the displacement expansions of $U_{1,0}$ and W_{ij}, and determine the linear dependence of the temperature contribution to $\bar{W}$. This anharmonic correction, however, becomes comparable with the main harmonic contribution at sufficiently low temperatures. Since at these temperatures the second-approximation contribution to the internal energy is small, for the necessary estimates of the temperature dependence of $\bar{W}$, it is necessary to turn to direct computer calculations.

As a simple algorithm of a direct calculation of $\bar{W}$, we used a method similar to that described in [3]. Gaussian quadrature equations were used with four sites in each variable and a weight $\exp(-x^2)$. The integrand was calculated at $4^6 = 4096$ points. The accuracy of the calculation was estimated by comparing the harmonic value of $\bar{W}$ with extrapolation results to $T = 0$, and was 1-2% for $\rho^* \geq 1.1$. In calculating $U_{1,0}$ we used a portion of the lattice with 64 nearest neighbors to the particle under consideration. The results of calculating the quantity $\bar{W}$ for a Lennard-Jones crystal with an fcc lattice are given in Table 1. The second-approximation correction to the thermodynamic function was calculated by a finite-difference method. Account of binary correlations in pressure calculations gives a very small correction, particularly at low temperatures. Comparison with the deviation of the Monte Carlo data from the first approximation [4] shows that except for the isotherm $T^* = 2.74$ the correction under consideration is within the random error of the computer experiment. We note that a direct calculation of $\bar{W}$ leads to a small positive contribution to pressure, and noticeably improves the agreement with Monte Carlo data at $T^* = 2.74$, while the harmonic approximation gives a negative correlation contribution to pressure.

A more important effect provides a correlation contribution to the internal energy

$$\Delta U_{\text{cor}} = \Theta \frac{\partial}{\partial \Theta} \bar{W}.$$

TABLE 3. Comparison of Calculation Results of the Specific Volume of Xenon with Experimental Data [7] (cm^3/mol)

P, bar	$T=100$			130			150		
	V_{cal}	v_{ex}	δ, %	V_{cal}	V_{ex}	δ, %	V_{cal}	v_{ex}	δ, %
0	36,76	36,65	0,2	37,74	37,56	0,5	38,50	38,15	0,8
500	35,98	35,93	0,1	36,85	36,60	0,6	37,47	—	—
1000	35,39	35,31	0,2	36,11	35,92	0,5	36,62	36,36	0,7
2000	34,36	34,25	0,3	34,94	34,72	0,6	35,34	35,11	0,7
4000	32,92	32,78	0,4	33,31	33,05	0,7	33,59	33,30	0,8
6000	31,87	31,66	0,6	32,17	31,82	1,0	32,37	32,05	0,9
8000	31,05	30,78	0,8	31,27	30,87	1,2	31,44	31,10	1,1
10000	30,36	29,98	1,2	30,55	30,11	1,4	30,69	30,39	1,0

TABLE 4. Comparison of Calculated Volumes of Solid Argon at the Melting Line with Experiments (cm^3/mol)

T, °K	P, kbar	V_{cal}	V_{ex}	δ, %	Ref.
90	0,25	24,62	24,46	+0,65	[8]
100	0,68	24,26	24,24	+0,08	
120	1,63	23,59	23,66	—0,30	
140	2,66	22,99	23,08	—0,39	
180	4,98	21,96	22,04	—0,36	
220	7,59	21,12	21,20	—0,38	
260	10,44	20,41	20,50	—0,44	
198,15	6,4	21,56	21,437	+0,57	[9]
223,15	7,9	21,06	20,977	+0,40	
248,15	9,7	20,61	20,549	+0,30	

This effect is particularly important at high temperatures, since the calculation is proportional to T^2. Thus, at $T^* = 2.74$ it consists of 5% of the total potential energy of the crystal, and taking it into account practically leads to complete agreement with results of the computer experiment.

The second-approximation correction to the entropy is more noticeable. The direct calculation results somewhat exceed the harmonic estimate, and provide an approximately constant value near 0.3k. This is a quite significant contribution. Thus, e.g., for solid argon at the triple point, it is 7% of the absolute entropy value. Therefore, any theory pretending to provide quantitative description of the whole complex of thermodynamic properties of the crystal must take into account the correlation between particle displacements.

Thus, the second-approximation estimates performed make it possible to directly apply the method developed in [1, 3] to real crystals at high pressures and temperatures.

The solidified rare gas crystals are the simplest type of molecular crystals. They all possess fcc lattices; the interaction energy of their atoms is purely Van der Waals, nearly pair additive, and is well approximated by a sum of pair Lennard-Jones potentials. For these reasons they have been the traditional object to studying various theoretical results and models. Besides, due to the prospective use of solidified forms of the zeroth group as high-pressure media, it has become necessary to calculate their properties at pressures up to dozens of kilobars and at temperatures significantly exceeding the normal melting temperature. Experimental data under these conditions are either not available, or very few and insufficient. This was the reason that in [4] an attempt was undertaken to calculate and tabulate the properties of the solidified rare gases at high pressures and temperatures up to 300°K. Below we discuss several results of these calculations.

For a number of reasons the use of the method for real crystals may not be totally adequate. This firstly refers to the presence of vacancies and other crystalline structure defects in the latter, leading to certain divergences with experimental data near the triple point. This region, however, is quite small and relates to the low-pressure region. Besides, the hypothesis of pair additivity of the potential energy does not always correspond to reality, and the potential interaction energy of a pair of atoms is not always properly given by the Lennard-Jones equation. This leads to the consequence that the potential parameters ε and σ used in the literature differ somewhat from each other. Under these conditions, it is often convenient to fit these parameters, so as to obtain best description of some properties in some temperature region. This method, however, is not acceptable from the point of view of verifying the suitability of the method suggested and possible extrapolation to the limits investigated experimentally. In this connection we did not attempt an optimization of the parameters ε and σ, but adopted the values used in [5] to calculate elastic constants of the solidified rare gases. These values are given in Table 2, while the parameters for radon were adopted from the data of [6] with use of the law of corresponding states.

Connected with the absence of especially fitted parameters in the calculation performed, comparison of its results with experimental data becomes particularly significant. Unfortunately, as already noted, experimental data are mostly available on sublimation lines, and measurements at high pressure are quite scarce and refer almost exclusively to thermal properties of crystals.

TABLE 5. Comparison of First and Second Approximations to Solid Argon Entropy at the Melting Line with Results of Experimental Data [8, 10]

T, K	$S^{(1)}/k$	$\overline{W}$	$\Theta \frac{\partial}{\partial\Theta} \overline{W}$	$S^{(2)}/k$	S/k [10]	S/k [8]
90	4,55	0,25	0,04	4,84	4,776	4,78
100	4,71	0,26	0,04	5,01	4,995	4,99
120	4,98	0,26	0,04	5,28		5,30
140	5,20	0,26	0,04	5,50		5,54
180	5,55	0,27	0,04	5,86		5,89
220	5,81	0,27	0,04	6,12		6,14
260	6,02	0,28	0,04	6,34		6,32

The specific volume of argon and xenon was experimentally studied in some more detail. Tables 3 and 4 compare results of our calculations with experimental data [7-9]. The average deviation with measurements of the specific volume of solid xenon in the temperature range 100-150°K and pressures up to 10 kbar is 0.7%, and the maximum deviation is 1.4%. In this case some enhancement of the deviation is observed when pressure increases, related to the too sharp increase in repulsion at small distances in the Lennard-Jones potential (12-6). This occurs mostly at low temperatures, where the elasticity of the static lattice provides the main contribution to the pressure. Indeed, comparison of the calculated and experimental values of the specific volume of argon at the melting line (Table 4) shows good agreement up to 15 kbar, corresponding to $T = 320°K$. Thus, the method of calculation guarantees good accuracy of the predicted specific volume of the heavy rare gases at high pressures and temperatures.

Of all the caloric functions, only the crystal entropy, found in equilibrium with the liquid or the vapor, can be calculated easily from the experimental data. Table 5 compares results of our calculations with the data of [8, 10]. As is seen, good agreement is achieved only with inclusion of the second-approximation theory. Binary correlations provide a quite noticeable contribution, up to 30% of the maximum value of the collective entropy [2].

The weak variation of the second-approximation contribution to entropy with temperature is in agreement with the conclusion drawn in [3] on the small effect of correlation on heat capacity of a crystal. Thus, the comparison performed demonstrates the usefulness of the calculation method used and its adequacy for predicting a whole complex of thermodynamic functions of simple molecular crystals in the regions of high temperatures and pressures and strong anharmonic effects.

NOTATION

P, pressure; P_0, elasticity of a static lattice; $\Theta \equiv kT$, statistical temperature; v, specific volume (volume of an elementary unit cell); $\rho = \sigma^3/v$, reduced density; $U_{s,0}$, potential energy of s particles in the field of a static lattice; W_{ij}, correlation energy of a pair of oscillating particles; m, particle mass; h, Planck constant; k, Boltzmann constant; ε, depth of the potential well; σ, molecular diameter; v_f, free volume; $\overline{W}$, correlation energy; $T^* = kT/\varepsilon$, reduced temperature; A, free energy; U, internal energy; and S, entropy.

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THERMOPHYSICAL PROPERTIES OF IRON, NICKEL, AND ALLOYS BASED ON THESE METALS IN THE VICINITY OF PHASE TRANSFORMATIONS

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A method is proposed for obtaining undistorted values of the temperature dependence of the thermophysical properties of metals and alloys in the vicinity of of phase transformations, based on taking into account directly the thermal inertia of the system.

In studying phase transformations, calorimetric methods, based on their being modeled by independent sources of heat energy, including the method of scanning adiabatic calorimetry, are most often used. Together with the advantages (rapidity, possibility of realizing a wide dynamic range), this method has the disadvantage that the results of the measurements obtained with its help are greatly distorted due to the thermal inertia of the system.

In the present work, we propose a method for obtaining undistorted values of the temperature dependence of thermophysical properties of metals in the vicinity of phase transformations, based on taking into account the thermal inertia of the system in an operational manner. This method permits using the temperature dependence of thermophysical properties for identifying the types of processes occurring [1].

The actual investigations were carried out in a vacuum (10^{-5} mm Hg) using an adiabatic scanning calorimeter, developed at the Institute of Metal Physics of the Academy of Sciences of the Ukrainian SSR [2], using standardized cylindrical specimens, heated by internal microheaters with heating rates of 1-10 deg/min, scanning from 300 to 1500°K, and a precision of $(\Delta T)_{max}/T = 0.1\%$, in maintaining the regular regime of the second kind relative to the maximum deviation of the temperature from the set value and of $(\Delta b/b)_{max} = 0.1\%$ relative to the maximum deviation of the heating rate $b = dT/dt = const$ from the given value. The limiting systematic error of the measurements not accounted for was $\delta C_p/C_p \leq 3.5\%$.

Let us examine a hollow cylindrical specimen with an internal heater, surrounded by a protective shell, the temperature of which was maintained equal to the temperature of the specimen surface programmed according to $T_p = T_i + b_p t$ (where $b_p = dT_p/dt$) in order to create quasiadiabatic conditions. Under these conditions, all of the heat power $P_p(t)$ input to the specimen goes into heating it.

When the regular regime is strictly observed, without taking into account thermal inertia, the temperature dependence of the heat capacity $C_p(T)$ is described by the expression

$$C_p(T) = P_p(t)/b_p. \tag{1}$$

In actuality, in order to transmit heat from the heater to the specimen, a finite time, which is determined by the thermal inertia of the specimen $\tau = C_p/\gamma$ (γ is the coefficient of

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