FLUCTUATIONS OF THE LATTICE CONSTANT IN CRYSTAL

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The aim of the presented paper is to show that fluctuations of the lattice constant play an essential role in theory of the equation of state for crystals near their crystalline phase transition temperatures. The influence of fluctuations is considered in approximation of homogeneous subsystems according to the cell model suggested by Smoluchowski. The mean square fluctuation is derived by taking into account the Morse potential in pseudo-harmonic approximation. It has been shown that taking into account fluctuations of the lattice constant changes the relation among the variables P, V and T near the critical point.

1. Introduction

It has been shown [1] that taking into consideration the particle density fluctuations in the derivation of the equation of state for a fluid system leads to the corrected equation of state and gives better agreement with experimental data than other theories. Even in rough approximation the fluctuation correction to the van der Waals equation gives the value of the critical ratio $Z_c \leqslant 0.33$ which is more close to an average experimental value for several gases $Z_c = 0.292$ than other theoretical results. It has been shown that the density fluctuations are responsible for the phenomenon of phase transition in a fluid system and enables us to explain the mechanism of condensation.

The fluctuations are believed to be negligible from the macroscopic point of view. Thus, the fluctuations are usually neglected in the derivation of thermodynamic relations between physical quantities describing a system. On the other hand, it is a well known fact that the fluctuations become abnormally large in the vicinity of the critical point and they are responsible for critical phenomena such as critical opalescence or critical scattering of neutrons. In particular, the crystal lattice symmetry of fluctuations plays an important role in the investigations of critical scattering of X-rays observed in dielectric crystals or in crystalline binary alloys [2, 3]. The lattice constant fluctuations in crystal correspond to the density fluctuations in a liquid system. The aim of this paper is to answer the question how the lattice constant fluctuations can influence the equation of state for crystal and, in particular, how they change its behaviour in the phase transition region.

From the point of view of statistical physics the equation of state can be derived by

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means of the thermodynamic functions calculated on the basis of the Hamiltonian for a given system. In the case of the equation of state for crystal it is necessary to take into account the Hamiltonian including an anharmonic nature of interatomic interactions. Usually the anharmonicity of lattice vibrations is considered by means of the perturbation theory in cubic or fourth order approximation. Recent investigations show, however, that this approach cannot be applied to the description of crystal properties near the phase transition point when the anharmonic effects are sufficiently large. Therefore, in order to find the theory convenient for proper description of phase transition in crystal we apply the self-consistent method based on the equation of motion for the double time thermodynamic Green's function [4] in its zeroth order approximation, which is known as the pseudoharmonic approach [5]. The main idea of the pseudoharmonic theory consists in assumption of the self-consistent phonon field in which phonons can propagate as the collective excitations appearing in a crystal. So, from the physical point of view, this approximation is equivalent to the molecular field theory. In other words we can say that the physical model of a crystal applied for our considerations is analogical to the model discussed in the case of van der Waals theory of a liquid system or to the Weiss approximation for a ferromagnet.

Detailed calculations are carried out for the Morse potential of crystal interactions [6] applied to a crystal with simple cubic symmetry.

2. Fluctuation model of a crystal near the critical point

In order to formulate the fluctuation model of a system near the phase transition temperature we apply the idea conceived by Smoluchowski [7] in connection with his theory of critical opalescence. The starting point consists in the observation that the system in question becomes inhomogeneous since fluctuations of the lattice constant grow rapidly in any region of crystal when the critical point is approached. The system can be conceived as one composed of N_f cells in which the lattice constant differs from the mean one. The nteractions between cells are taken into account only by the interactions between neighbours of atoms lying at the boundary of a given cell. This assumption is equivalent to the statement that the various cells are not correlated. Therefore, for each cell the rest of a crystal can be treated as a reservoir. The cells treated as the subsystems immersed in reservoir form some topological configuration at a given moment of time, but their dimensions and values of the local lattice constant undergo changes in time due to the dynamical nature of the fluctuations. It is generally postulated that all thermodynamic functions exist for each cell. The subsystem remains in a non-equilibrium state with respect to the reservoir, but we can assume a local equilibrium. In other words, all physical quantities of the subsystem are given by the corresponding equilibrium functions in which the equilibrium variables are replaced by the local instantaneous variables [8, 9]. Thus, any additive quantity A of the system can be expressed by a sum over these quantities of the subsystems

$$A = \sum_{i=1}^{N_f} A_i. \tag{1}$$

In order to calculate A_i an arbitrary phenomenological or microscopic model of a system and the standard theory of fluctuations can be applied.

This physical model of the system near the critical point has been used to derive the equation of state for a fluid system [1] and a magnetic system [10] as well as for calculating the specific heat of a ferromagnet above T_c [11]. A similar model has been suggested by Rolov [12].

3. *Influence of the lattice constant fluctuations on interatomic interaction*

In first approximation we assume that the local fluctuations of the lattice constant are homogeneous. Neglecting a possible space distribution of the lattice constant within fluctuation, we can express the local value of the lattice constant as follows:

$$l_i = \bar{l}(1+\delta_i), \tag{2}$$

where δ_i denotes the lattice constant fluctuation in the i-th subsystem and $\bar{l}$ is the all over average and has the meaning of equilibrium value. So, l_i denotes the instantaneous value of $\bar{l}$ in the i-th subsystem averaged over the space of fluctuation. Since the length of a crystal is assumed to be independent of the configuration of fluctuations we can write condition for the average value of the lattice constant in the form:

$$\sum_i \delta_i = 0. \tag{3}$$

Condition (3) does not exclude the possibility that the mean lattice constant $\bar{l}$ depends on the mean square fluctuation determined as

$$\langle \delta^2 \rangle = \frac{1}{N_f} \sum_i \delta_i^2. \tag{4}$$

According to the pseudoharmonic approximation we assume that the interactions in the homogeneous subsystem can be expressed in terms of the effective Morse potential as follows [6]:

$$\tilde{\varphi}_i(l_i, y) = D\left[e^{-12\left(\frac{l_i}{r_0}-1\right)}e^{2y} - 2e^{-6\left(\frac{l_i}{r_0}-1\right)}e^{\frac{y}{2}}\right] \tag{5}$$

where D is the dissociation constant and r_0 denotes the equilibrium position in the case of harmonic interactions. Thus, r_0 does not depend on temperature and remains a parameter of the theory. The parameters D and r_0 take the same values for all the subsystems. It results from the fact that the static forces in crystal do not fluctuate while fluctuation is created under the action of a random force. The variable y is related to the mean square relative displacement of neighbouring atoms and can be expressed by means of the harmonic phonon frequencies $\omega_\lambda^0(h)$ calculated for the polarization branch λ and the wave vector h

belonging to this branch. On the basis of calculations carried out in the paper [6] we can write:

$$y = \frac{1}{Nr_0^2 f(\bar{l}) f(r_0)} \sum_{\lambda h} \omega_\lambda^0(h) \operatorname{cth} \frac{f(\bar{l})\omega_\lambda^0(h)}{2f_0(r_0)k_B T}, \tag{6}$$

where T denotes the temperature of a system, k_B is the Boltzmann constant, N — the number of atoms and $f_0(r_0)$ stands for the harmonic strength constant. The pseudoharmonic strength constant $f(\bar{l})$ can be written as

$$f(\bar{l}) = \frac{d^2\tilde{\varphi}(\bar{l})}{d\bar{l}^2}. \tag{7}$$

The procedure leading to formula (6) is based on the assumption that phonons are propagated through the homogeneous system in which the inhomogeneities due to fluctuations are averaged over the space of crystal. So, the influence of fluctuations on the average phonon field is considered by means of the mean number of phonons calculated for crystal with the lattice constant dependent on the mean square fluctuation given by (4). In this way we can consider the influence of local fluctuations on the overall properties of crystal in the molecular field approximation.

The lattice constant fluctuations create the lines of discontinuity of the lattice constant at the boundaries of fluctuation cells. Since the fluctuations are of the dynamical character these lines move inside a crystal. Under some circumstances this movement can be very slow and such a case corresponds to a crystal with dislocations which are originated from the lattice constant fluctuations.

4. Mean square fluctuation

In order to give a more detailed discussion of the problems mentioned in the previous section one should write an explicit form of the mean square fluctuation of the lattice constant. In this aim we apply the method developed by Smoluchowski [7] for calculating the probability of occurrence of a fluctuation. The general formula for the mean square fluctuation has the form:

$$\langle \delta^2 \rangle = \int_{\delta_{\min}}^{\delta_{\max}} \delta^2 \exp\left[-L(\delta)/k_B T\right] d\delta \Big/ \int_{\delta_{\min}}^{\delta_{\max}} \exp\left[-L(\delta)/k_B T\right] d\delta, \tag{8}$$

where $L(\delta)$ denotes the work necessary to create the fluctuation described by the parameter δ. The limits $\delta_{\max}$ and $\delta_{\min}$ in Eq. (8) are connected with the physically possible values of δ. Condition (3) requires $\delta_{\max} = -\delta_{\min} = \delta_m$ if only the probability distribution is an even function of δ. In the case of temperature and volume as the independent variables, the work L can be expressed by the change of the Helmholz free energy. Let us assume that the subsystem is being compressed from its equilibrium volume v to a volume v_1 while the reservoir is being expanded from V to V_1. Since the volume of the reservoir is much larger than the volume of the subsystem, we can also assume that the pressure

in the reservoir remains constant and equal to the equilibrium value $P(V)$ during the whole process when the fluctuation is being created. Thus, the work L can be expressed as follows:

$$L(\delta) = -\int_{v}^{v_1} [P(v)-P(V)]dv, \tag{9}$$

with the temperature of the subsystem kept constant since the fluctuations in temperature and the lattice constant can be regarded as statistically independent. According to our general assumptions the local pressure is determined by the equation of state for a homogeneous system being in the equilibrium state. In order to find $P(v)$ we apply the equation of state for crystal obtained by Siklós [6]:

$$P(V) = -\frac{12D}{r_0 l^2} x(l)\,[e^{y/2}-x(l)e^{2y}], \tag{10}$$

where $x(l) = \exp[-6(l/r_0-1)]$ and $V = Nl^3$. Taking into account relation (2) we have

$$v_1 = N_0\bar{l}^3(1+\delta)^3, \tag{11}$$

when N_0 denotes the number of atoms in the subsystem. It results from our physical model that the mean number of fluctuations N_f is equal to the ratio of all atoms to the mean number of atoms $\bar{N}_0$ in the fluctuation. The number $\bar{N}_0$ can be determined theoretically [13].

In the spirit of the molecular field approximation the variable y given by equation (6) does not depend directly on δ. So, using relations (2) and (10) we have

$$P(v) = -\frac{12}{r_0\bar{l}^2} x(\bar{l}) \frac{e^{-6\frac{\bar{l}}{r_0}\delta}}{(1+\delta)^2} [e^{y/2}-x(\bar{l})e^{-6\frac{\bar{l}}{r_0}\delta}e^{2y}]. \tag{12}$$

Substituting equation (12) into (9) and next carrying out the integration over δ instead of v, where $dv = 3N_0\bar{l}^3(1+\delta)^2 d\delta$, we obtain

$$L(\delta) = 36D\frac{N_0\bar{l}}{r_0}\left\{x(\bar{l})\,e^{y/2}\left[\frac{1-e^{-6\frac{\bar{l}}{r_0}\delta}}{6\frac{\bar{l}}{r_0}} - \tfrac{1}{3}((1+\delta)^3-1)\right]\right.$$

$$\left. -x(\bar{l})e^{2y}\left[\frac{1-e^{-12\frac{\bar{l}}{r_0}\delta}}{12\frac{\bar{l}}{r_0}} - \tfrac{1}{3}((1+\delta)^3-1)\right]\right\}. \tag{13}$$

In the approximation to the linear terms with respect to δ^2 we obtain

$$L(\delta) = 36D\frac{\bar{l}}{r_0} N_0 x(\bar{l})\left[x(\bar{l})e^{2y}\left(1+6\frac{\bar{l}}{r_0}\right) - e^{y/2}\left(1+3\frac{\bar{l}}{r_0}\right)\right]\delta^2. \tag{14}$$

Thus, the probability distribution function for occurrence of fluctuation described by the parameter δ takes the form of the Gaussian type

$$p(\delta)d\delta = \exp\left[-N_0\alpha\delta^2/k_BT\right]d\delta, \tag{15}$$

where

$$\alpha = 36D\frac{\bar{l}}{r_0}x(\bar{l})\left[x(\bar{l})e^{2y}\left(1+6\frac{\bar{l}}{r_0}\right)-e^{y/2}\left(1+3\frac{\bar{l}}{r_0}\right)\right]. \tag{16}$$

Using equations (8) and (14) we obtain the following expression for the mean square fluctuation:

$$\langle\delta^2\rangle = \frac{k_BT}{2\bar{N}_0\alpha}\left[1-\frac{2\delta_m\exp\left(-\frac{\bar{N}_0\alpha}{k_BT}\delta_m^2\right)}{\sqrt{\frac{\pi\bar{N}_0\alpha}{k_BT}}\,\varphi\left(\sqrt{\frac{\bar{N}_0\alpha}{k_BT}}\,\delta_m\right)}\right], \tag{17}$$

where φ is the probability integral. The quantities $\bar{N}_0$ and δ_m are treated in this paper as parameters of the theory.

On the other hand, it is known from the theory of fluctuations [9] that the probability index is related to the isothermal compressibility and vanishes at T_c. Looking for the asymptotic behaviour of $\langle\delta^2\rangle$ we obtain from (17) for $\alpha \to 0$ as follows:

$$\langle\delta^2\rangle_{T\to T_c} = \tfrac{1}{3}\delta_m^2. \tag{18}$$

For temperatures away from T_c the probability distribution function is sharp and rapidly convergent. Then the limits $\pm\infty$ in equation (8) can be assumed and we obtain the well known result:

$$\langle\delta^2\rangle = \frac{k_BT}{2\bar{N}_0\alpha}. \tag{19}$$

The mean square fluctuation given by (19) is divergent for $T \to T_c$, but the assumption at which result (19) has been obtained is not valid near the critical point. When the critical temperature is approached the probability distribution function becomes more and more flat because of the decrease of probability index.

5. Equation of state for inhomogeneous crystal system

Using general relation between the external pressure and the interaction potential [6] we can write the following formula for the average pressure in the total system composed of N_f homogeneous fluctuations of the lattice constant

$$P = -\frac{\bar{l}}{V}\left\langle\frac{\partial\tilde{\varphi}_i(l_i, y)}{\partial l_i}\right\rangle. \tag{20}$$

According to (5) the pseudoharmonic potential $\tilde{\varphi}_i$ is the nonlinear function of l_i being the function of δ. Thus, the statistical average $\langle \tilde{\varphi}_i'(l_i, y)\rangle$ is certainly a function of $\langle \delta^2 \rangle$. Substituting (5) into (20) we obtain in approximation to the linear terms with respect to $\langle \delta^2 \rangle$ as follows:

$$P = -\frac{12D}{r_0 \bar{l}^2}\left[e^{y/2} - x(\bar{l})e^{2y}\right]x(\bar{l})$$

$$+\frac{72D}{r_0 \bar{l}^2}x(\bar{l})\left[e^{y/2}\left(1-\frac{\bar{l}}{r_0}\right) - 2x(\bar{l})e^{2y}\left(1-2\frac{\bar{l}}{r_0}\right)\right]\langle \delta^2 \rangle. \tag{21}$$

The second term of Eq. (21) expresses the correction to the equation of state for crystal given by the lattice constant fluctuations. The mean lattice constant $\bar{l}$ as a function of $\langle \delta^2 \rangle$ is determined by means of equation (21).

The local, isothermal change of pressure due to the lattice constant fluctuation with the parameter δ is equal to the difference

$$\Delta P = P(v_1) - P(V), \tag{22}$$

where $P(v_1)$ and $P(V)$ are determined by equations (12) and (10) correspondingly. Considering equation (22) one can find δ_c as the value of δ for which the local change of pressure ΔP due to the lattice constant fluctuation is equal to zero. This change would be negative for $\delta > \delta_c$, which would mean negative local compressibility. Such a situation corresponds to the local phase transition. Even far away from the critical temperature there is a finite probability that the fluctuation corresponding to a new phase can be created in a small element of volume for a very short period of time, since the probability distribution function (15) is determined for all values of δ even away from the critical region. The whole system, however, becomes unstable mechanically when the mean square fluctuation is equal to the square of the critical fluctuation δ_c. Thus, we suggest the criterion of stability in the general form [1]

$$\langle \delta^2 \rangle = \delta_c^2. \tag{23}$$

The stability criterion (23) is connected with local mechanical instability but it does not mean that the overall isothermal compressibility must be negative. Clearly, the local and overall compressibilities are different [14]. The local isothermal compressibility can be found from equation (12) while the overall compressibility should be calculated from the equation of state (21) which is averaged over the all fluctuations.

6. *Conclusions*

Our aim has been to show that the inhomogeneities due to fluctuations of the lattice constant should be taken into consideration in the derivation of the equation of state for crystal. The lattice constant fluctuations give corrections to the equation of state particularly in the vicinity of the phase transition. It is known that the experimental data deviate from the function fitted to results of rigorous theories in the immediate vicinity

of the critical point (e.g. [15]), that means for reduced temperature sufficiently small, less than 10^{-4} in order. It is usually assumed that these deviations are caused by sample inhomogeneities like impurities or crystal defects. Near the critical point the fluctuations create inhomogeneities in any physical system undergoing a phase transition. Since the dimensions of fluctuations grow rapidly when T approaches T_c, in the immediate vicinity of the critical point the fluctuations are a main source of inhomogeneities. Due to the dynamical nature of fluctuations we observe rather "diffuse" phase transition instead of "sharp" phase transition. This fact enables us to explain some diversity of meaning or renormalization of the critical point exponents in the immediate vicinity of the critical temperature.

The aim of the paper is to give a physical picture of how the lattice constant fluctuations influence the overall properties of crystal, and not to present the exact theory of lattice vibrations. Therefore, we limited our considerations of the fluctuation model of crystal to the case of simple cubic lattice and interatomic interactions in the form of the Morse potential. Some numerical estimations obtained on the basis of our physical model of a crystal in the case of pressure equal to zero give reasonable results [16]. Because the mean square fluctuation strongly depends on temperature near the critical point, one can expect that the critical properties deduced from equations (21) and (23) will be altered in comparison with the case when fluctuations are neglected. The detailed numerical analysis would be valuable in the case of real crystal lattice and more realistic form of the interaction potential. Our results have only illustrative character but we hope that they can be treated as the starting point to further development of the theory of phase transitions in crystals.

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