

# CORRELATION PROPERTIES AND THE STRUCTURAL INSTABILITY OF THE TWODIMENSIONAL ANHARMONIC CRYSTAL. THE VIRIAL APPROACH

V. K. PERSHIN and I. S. GERSHT

*Ural Polytechnical Institute, 620002 Sverdlovsk, USSR*

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In terms of the virial theorem for an arbitrary two-dimensional lattice a self-consistent system of equations is developed that allows its dynamics and the temperature evolution to the stability limit to be investigated in the nearest neighbour approximation. Contrary to the traditional approach the relative correlation functions of the longitudinal and transversal displacements of particles and the force constants corresponding to them are introduced. The topology of the virial surface and the evolutional trajectory of the lattice state, the temperature behaviour of the longitudinal and transversal force constants of the lattice are discussed. The irregular growth of the adiabatic elastic modulus with temperature, and the change of sign of its derivative observed experimentally in cubic crystals are explained. It is shown that there exists a temperature range where the system stability is achieved by the redistribution of the kinetic energy between the longitudinal and transversal displacements of particles. It is established that the instability of the lattice relative to its longitudinal oscillations is the main cause of its structural re-arrangement in the high temperature range in spite of the more rapid development of the transversal oscillations with temperature increase.

## 1. Introduction

The balance between the kinetic energy of particles and the energy of their coupling in the lattice is destroyed during the structural transitions in crystals [1] which is why the virial theorem establishing the relation between these most important characteristics of the system is of great significance regarding the stability of the crystalline state [2]. The advantage of the use of the virial equation was proved by its having given the best practical results for weakly interacting systems [3]. In spite of this, however, the application of the virial theorem for investigating the properties of crystals and in particular the mechanisms of their structural instability is still at its very beginning.

In the present paper the mechanisms of the formation of the two-dimensional lattice instability due to temperature increase are discussed in terms of a self-consistent pseudoharmonic approximation based on the virial theorem. The successive introduction of the correlation functions for different types of displacements gives the possibility to establish the importance of each of them for instability formation.

According to the Landau—Peierls theorem the system of atoms in the plane forms a crystalline lattice at  $T=0$  K only. Long-range order of the lattice is destroyed by long-wave fluctuations at any non-zero temperature. Strictly speaking, such a system is not a crystalline one and it can be considered as such only within the range of distance  $R$  [4]

$$R = a \exp(\pi mu^2/2kT),$$

where  $a$  is the average distance between the particles;  $u$  is the average sound velocity and  $m$  is the mass of the atom.

The absence of long-range order does not rule out the possibility of structural instability in such systems, a fact confirmed by high temperature expansion [5, 6], the correlation functions technique [7], computer simulation [8, 9] and the self-consistent phonons method [10, 11].

Further, for simplifying the calculations the case of the high temperature limit will be considered only where the theorem of the equipartition of kinetic energy over the degrees of freedom of particles is fulfilled. If the mass of atoms is large enough then the lowest temperatures can be involved in this classical range [12].

## 2. Self-consistent system of equations

Let us consider a combination of the atoms interacting with each other by the pair central forces in the plane. The Hamiltonian of such a system has the usual form

$$H = K + U,$$

where

$$K = \sum_j \left( -\frac{\hbar^2}{2m} \nabla_j^2 \right), \quad U = \frac{1}{2} \sum_{k,1} \Psi(|\mathbf{r}_k - \mathbf{r}_1|).$$

Let us write the virial theorem for an arbitrary degree of freedom of the atom "0" located at the origin of the coordinate system

$$2m \langle (\dot{u}_0^i)^2 \rangle = \left\langle u_0^i \frac{\partial U}{\partial u_0^i} \right\rangle, \quad i = 1, 2;$$

where  $u_0^i$  is the  $i$ -component of the translational displacement of the atom from the equilibrium position. For the high temperature limit, by expanding the potential energy  $U$  in this relation into the infinite series over displacements and presenting the multidimensional correlation functions in the pseudo-harmonic approximation [13] we get

$$kT = - \sum_{i', \mathbf{n}} x_{0\mathbf{n}}^{ii'} \Phi_{0\mathbf{n}}^{ii'}, \quad i, i' = 1, 2; \quad (1)$$

where  $x_{0\mathbf{n}}^{ii'} = \langle (u_0^i - u_{\mathbf{n}}^i)(u_0^{i'} - u_{\mathbf{n}}^{i'}) \rangle$ ,  $\mathbf{n}$  is the radius-vector of a certain lattice site and

$$\Phi_{0\mathbf{n}}^{ii'} = \left\langle \frac{\partial^2 U}{\partial u_0^i \partial u_{\mathbf{n}}^{i'}} \right\rangle = \frac{\partial^2}{\partial u_0^i \partial u_{\mathbf{n}}^{i'}} \exp \left[ -\frac{1}{4} \sum_{\mathbf{p}\mathbf{p}'} x_{\mathbf{p}\mathbf{p}'}^{jj'} \frac{\partial^2}{\partial u_{\mathbf{p}}^j \partial u_{\mathbf{p}'}^{j'}} \right] U \quad (2)$$

is the force constant defined by the functions  $x_{0\mathbf{n}}^{ii'}$  included in Eq. (1). Each of these functions can be determined by the spectral theorem

$$x_{0\mathbf{n}}^{ii'} = \frac{1}{mN} \sum_{\mathbf{k}, j} \frac{e_{\mathbf{k}j}^i e_{\mathbf{k}j}^{i'}}{\omega_{\mathbf{k}j}} (1 - e^{-i\mathbf{k}\mathbf{n}}) \text{cth} \frac{\omega_{\mathbf{k}j}}{2kT}, \quad (3)$$

where  $N$  is the number of particles;  $\mathbf{k}$  is the quasi-wave vector;  $j$  is the number of the oscillation branch.

The force constants (2) are calculated for the equilibrium state of the lattice. Therefore, so that the system of equations (1)–(3) becomes closed to all unknown parameters it should be added to the conditions of the lattice equilibrium.

The frequencies of the excitations of the crystal,  $\omega_{\mathbf{k}j}$ , included in (3) and the components of the eigenvectors corresponding to them,  $e_{\mathbf{k}j}^i$ , are determined by the relation

$$\text{Det} \| D_{ii'}(\mathbf{k}) - m\omega_{\mathbf{k}j}^2 \delta_{ii'} \| = 0, \quad (4)$$

$$m\omega_{\mathbf{k}j}^2 e_{\mathbf{k}j}^i - \sum_{i'} D_{ii'}(\mathbf{k}) e_{\mathbf{k}j}^{i'} = 0. \quad (5)$$

These parameters are also the functions of  $\{x\}$  since the elements of the dynamical matrix  $D = \| D_{ii'}(\mathbf{k}) \|$ ,

$$D_{ii'}(\mathbf{k}) = \sum_{\mathbf{n}} \Phi_{0\mathbf{n}}^{ii'} e^{i\mathbf{k}\mathbf{n}} \quad (6)$$

depend on the pseudo-harmonic force constants (2). Then, from Eq. (4) and (5), for an arbitrary lattice we have

$$m\omega_{\mathbf{k}j}^2 = \frac{1}{2} (D_{11} + D_{22} + (-1)^{j+1} \sqrt{(D_{11} + D_{22})^2 - 4(D_{11}D_{22} - D_{12}^2)}), \quad (7)$$

$$e_{\mathbf{k}j}^1 = \frac{D_{12}}{\sqrt{D_{12}^2 + (D_{11} - m\omega_{\mathbf{k}j}^2)^2}}; \quad e_{\mathbf{k}j}^2 = -\frac{D_{11} - m\omega_{\mathbf{k}j}^2}{\sqrt{D_{12}^2 + (D_{11} - m\omega_{\mathbf{k}j}^2)^2}}. \quad (8)$$

Since  $D_{12} = 0$  due to reflection symmetry for rectangular and square lattices  $e_{\mathbf{k}j}^i = \delta_{ij}$ . Going over to the high temperature limit  $\hbar\omega \ll kT$  in (3), integrating over the  $k$ -space and using also relations (7) and (8) we get

$$x_{0\mathbf{n}} = \frac{kT}{\pi^2} S \int_{(\mathbf{k})} \frac{1}{A(\mathbf{k})} ADA^T \text{Sin}^2 \frac{\mathbf{k}\mathbf{n}}{2} d^2k, \quad (9)$$

where  $x_{0\mathbf{n}} = \| x_{0\mathbf{n}}^{ii'} \|$  is the second order translational matrix;  $A$  is the  $\pi/2$ -rotation matrix;  $S$  is the area of the unit cell;  $A(\mathbf{k}) = D_{11}D_{22} - D_{12}^2$ .

The combination of relations (1)–(9) defines the self-consistent system of equations describing the dynamic state of a two-dimensional lattice for an arbitrary number of coordination spheres and in the particle interaction approximation. Let us note that the virial equations (1) are represented by the linear combinations formed accordingly of the elements of the correlation matrix (9) where the force constants (2)

are used as coefficients. Thus, they are not independent. Because of their clear physical meaning, however, the virial equations have a significant advantage over the spectral ones which is precisely why the virial theorem is applied for interpreting the mechanisms of the instability formation.

### 3. Square lattice in the approximation of the nearest neighbours

According to Eq. (1) the two-dimensional lattice with the arbitrary angle  $\theta$  between its axes is described by two virial equations in the nearest neighbour approximation. Each of them has four constants  $\Phi_{0\mathbf{n}}^{ii'}$  ( $i$  is the fixed index;  $\alpha$  is the number of the nearest neighbour) depending on the full set of correlations  $\{x_{0\mathbf{n}\alpha}^{k1}\}$ . The problem is essentially simplified for the case of the square lattice. Due to its symmetry we have

$$\Phi_{0\mathbf{n}\alpha}^{12} = \Phi_{0\mathbf{n}\alpha}^{21} = 0, \quad x_{0\mathbf{n}\alpha}^{12} = x_{0\mathbf{n}\alpha}^{21} = 0.$$

The consequence of the isotropy of the square lattice is the degeneration of the force constants

$$\Phi_{0\mathbf{n}_1}^{11} = \Phi_{0\mathbf{n}_2}^{22} = \Phi_1, \quad \Phi_{0\mathbf{n}_2}^{11} = \Phi_{0\mathbf{n}_1}^{22} = \Phi_2,$$

of the correlation functions

$$x_{0\mathbf{n}_1}^{11} = x_{0\mathbf{n}_2}^{22} = x_1, \quad x_{0\mathbf{n}_2}^{22} = x_{0\mathbf{n}_1}^{11} = x_2$$

and of the two virial equations into one. With the notations introduced before the latter can be written in the form

$$kT = -x_1 \Phi_1 - x_2 \Phi_2. \quad (10)$$

The correlation functions  $x_i$  describe the longitudinal ( $i=1$ ) and transversal ( $i=2$ ) displacements of particles and characterize the extent of corresponding oscillations in the crystal at the given temperature.

To form a closed system one of the following equations

$$x_i = -\frac{2kT}{\Phi_i} \arcsin G_i; \quad i=1, 2 \quad (11)$$

is to be added to Eq. (10), where  $G_i = \sqrt{\Phi_i/(\Phi_1 + \Phi_2)}$ . These values are obtained by calculating the elements of the dynamic matrix (6) in the nearest neighbour approximation

$$D_{ii'}(\mathbf{k}) = -4 \left( \Phi_{0\mathbf{n}_1}^{ii'} \sin^2 \frac{\mathbf{k}\mathbf{n}_1}{2} + \Phi_{0\mathbf{n}_2}^{ii'} \sin^2 \frac{\mathbf{k}\mathbf{n}_2}{2} \right)$$

and putting them into (9). Because the equation  $\Phi_2 = 0$  is strictly valid in the harmonic case in consideration of the first coordination sphere only [14] one can suppose that in the pseudo-harmonic approximation the inequality

$$|\Phi_2| \ll |\Phi_1| \quad (12)$$

is fulfilled. Taking into account the resulting approximative relation  $\arcsin G_2 \approx G_2$  after corresponding transformations we get:

$$\frac{x_1}{x_2} = \frac{\pi}{2} \left( \frac{\Phi_2}{\Phi_1} \right)^{1/2} - \frac{\Phi_2}{\Phi_1}. \quad (13)$$

The system of equations (10), (13) will be closed and self-consistent together with the condition of the equilibrium of the crystalline lattice only if

$$\delta \langle \Psi \rangle / \delta l = 0, \quad (14)$$

where  $\langle \Psi \rangle$  is the averaged isotropic pair interaction potential;  $l$  is the equilibrium parameter of the lattice in the self-consistent approximation.

Now we solve the system (10), (13), (14) for the Morse potential [15]

$$\Psi(r) = D(e^{-2g(r/r_0 - 1)} - 2e^{-g(r/r_0 - 1)}), \quad (15)$$

where  $D$  is the depth of the potential well;  $r_0$  is the equilibrium distance in harmonic approximation;  $g = \alpha r_0$ ,  $\alpha > 0$  are the potential parameters. The interaction potential corresponds to the conditions  $\Psi(r_{\pm}/r_0) = 0$ ,  $\partial^2 \Psi(r_{\pm}/r_0) / \partial^2 r = 0$ , where  $r_{\pm}/r_0 = 1 + \ln^2/g$ . From this consideration and from the analysis of the dependence of the half-width of the potential well on  $g$  it follows that the interaction forces in the lattice are of more long-range order now.

The averaged interaction potential  $\langle \Psi_{0n} \rangle$  corresponds to the equilibrium state and is calculated by the equation [13]

$$\langle \Psi_{0n} \rangle = \exp \left\{ \frac{1}{2} \sum_{ii'} x_{0n}^{ii'} V_{r_n}^i V_{r_n}^{i'} \right\} \Psi(r_n) \quad (16)$$

in the pseudo-harmonic approximation. Putting (15) into (16) and confining ourselves to the terms of order not less than  $x_{0n}^{ii'}/l_n^2$  we get the expression for the anisotropic averaged potential of an arbitrary lattice

$$\begin{aligned} \langle \Psi_{0n} \rangle = D(r/r) \sum_{p=1}^2 (-1)^{p+1} p \exp \{ -\alpha_p (l_n - r_0) - \\ - \sum_{i,j} \frac{\alpha_p}{2l_n} \left( \delta_{ij} - \frac{\alpha_p n^i n^j}{l_n} - \frac{n^i n^j}{l_n^2} \right) x_{0n}^{ij} \}, \end{aligned} \quad (17)$$

where  $\alpha_1 = 2\alpha(r/r)$ ,  $\alpha_2 = \alpha(r/r)$ ,  $|\mathbf{n}| = 1$ . For a square lattice  $\left( \sum_i n_x^i n_x^i = \delta_{\alpha\alpha} l^2, D(r/r) \equiv D, \alpha(r/r) \equiv \alpha \right)$  in the coordinate system  $n_x^i = \delta_{ix} l$ , we have

$$2\rho = \rho_0 + \sqrt{\rho_0^2 - 2x_{\perp}}, \quad (18)$$

$$\Phi_{\parallel} = (1 - x_{\perp}/\rho^2) \exp(-x_{\parallel}), \quad (19)$$

$$\Phi_{\perp} = (x_{\perp} - x_{\parallel}) \exp(-x_{\parallel}/\rho^2), \quad (20)$$

where

$$\rho = \alpha l, \quad \rho_0 = g + 3x_{||}/2, \quad x_{||} = \alpha^2 x_1, \quad x_{\perp} = \alpha^2 x_2, \\ \Phi_{||} = -\Phi_1/2D\alpha^2, \quad \Phi_{\perp} = -\Phi_2/2D\alpha^2.$$

Relations (19) and (20) confirm the correctness of the supposition expressed above by inequality (12). Putting them into Eq. (13), squaring the two parts of the equation obtained, up to first order of the parameter ( $x_{\perp}/\rho_0^2$ ) we can transform (13) to

$$x_{\perp}^3 + ax_{\perp}^2 + bx_{\perp} + c = 0. \quad (21)$$

The following notations are introduced in (21)

$$a = -x_{||} \left( 1 + \frac{8}{\pi^2} \right) < 0, \quad b = x_{||}^2 \left( \frac{20}{\pi^2} \right), \quad c = -x^2 \left( \frac{2\rho_0^2}{\pi} \right) < 0. \quad (22)$$

The real solution of Eq. (21) can be written [16] as:

$$x_{\perp} = f(x_{||}) = \frac{1}{3} \left( 1 + \frac{8}{\pi^2} \right) x_{||} + \left( \frac{2}{\pi} g \right)^{2/3} x_{||}^{2/3}. \quad (23)$$

Now, putting (19) and (20) into the virial equation (10) we get

$$\frac{kT}{2D} = \frac{F(x_{||}, x_{\perp})}{2D} = x_{||} \left( 1 - \frac{x_{\perp}}{\rho^2} \right) e^{-x_{||}} + x_{\perp} \frac{x_{\perp} - x_{||}}{\rho^2} e^{-x_{||}}. \quad (24)$$

The notations  $f(x_{||})$  and  $F(x_{||}, x_{\perp})$  have been introduced in Eqs (23), (24) for later convenience.

Using (23) in Eq. (24) and confining ourselves to the terms up to first order of the parameter  $x_{||}/g^2$  we get

$$\frac{kT}{2D} = \frac{F(x_{||}, f(x_{||}))}{2D} = x_{||} e^{-x_{||}} (1 + Q_g(x_{||})), \quad (25)$$

where

$$Q_g = \sum_{p=1}^3 c_p \left( \frac{x_{||}}{g^2} \right)^{p/3}, \\ c_1 = (2/\pi)^{4/3} \approx 0.55, \quad c_2 = -\frac{4}{3} \left( 1 - \frac{4}{\pi^2} \right) \left( \frac{2}{\pi} \right)^{2/3} \approx -0.59, \\ c_3 = -\frac{5}{9} \left( 1 + \frac{8}{\pi^2} \right) \left( 1 - \frac{8}{5\pi^2} \right) \approx -0.8.$$

The value of the correlation function  $x_c$  corresponding to the temperature of the dynamic instability of the lattice,  $T_c$ , is determined by the extremum condition for the function  $F(x_{||}, f(x_{||}))$

$$\frac{dF}{dx_{||}} = (1 + Q_g(x_{||})) (1 - x_{||}) + x_{||} \frac{dQ_g}{dx_{||}} = 0. \quad (26)$$

The estimations show that  $Q_g(x_{||}) \ll 1$  in the range of the physically reasonable values of  $g$  and  $x_{||}$  ( $2 \leq g \leq 10$ ,  $0 < x \approx 1$ ). Taking this into account we shall take the solution to equation (26) in the form  $x_c = 1 + \Delta_g$ ,  $\Delta_g \ll 1$ . This gives

$$x_{||c} = 1 + \sum_{p=1}^3 pc_p g^{-2p/3}. \quad (27)$$

Putting (27) into Eq. (23) we have

$$x_{\perp c} = \frac{1}{3} \left( 1 + \frac{8}{\pi^2} \right) + \left( \frac{2}{\pi} g \right)^{2/3} + Q_g, \quad (28)$$

where

$$Q_g = \left[ \frac{1}{3} \left( 1 + \frac{8}{\pi^2} \right) + \frac{2}{3} \left( \frac{2}{\pi} g \right)^{2/3} \right] \sum_{p=1}^3 \frac{1}{3} pc_p g^{-2p/3}.$$

Now, using (25), we can write the real expression for the instability temperature,  $T_c$ ,

$$T_c = T_A \left( 1 + \sum_{p=1}^3 c_p g^{-2p/3} \right),$$

where  $T_A = 2D/ke$  is the instability temperature of the lattice without taking the relative transversal correlations [18] into account. The contribution to the critical values of the correlation functions which is bound with the second and the third term in relations (27) and (28), respectively, is negative at  $g \geq 2$  and the modulus of its magnitude decreases with increasing  $g$ . The inequality  $T_c \leq T_A$  is valid for  $g \leq g_0 \approx 2.6$  where  $g_0$  is determined by the equation  $T_c(g) = T_A$ . For all the other values of  $g$  the reverse inequality is valid.

It is mentioned that the estimation of the parameters  $x_{||c}$ ,  $x_{\perp c}$ ,  $T_c$  is mathematically equivalent to the problem of the estimation of the conventional extremum of the function  $F = F(x_{||}, x_{\perp})$  if the coupling equation  $x_{\perp} - f(x_{||}) = 0$  is available [17–19].

#### 4. Topology of the virial surface and the evolution trajectory

In Fig. 1 the virial surface of the square lattice  $F = F(x_{||}, x_{\perp})$  is shown. The radius-vector  $\mathbf{r}$  of any point located on this surface and the unit tangent vector  $\boldsymbol{\tau}$  of the surface can be represented in the form

$$\mathbf{r} = \mathbf{i}x_{||} + \mathbf{j}x_{\perp} + \mathbf{k}F(x_{||}, x_{\perp}), \quad (29)$$

$$\boldsymbol{\tau} = \frac{d\mathbf{r}}{ds} = \frac{1}{\xi} \left( \mathbf{i} + \mathbf{j} \frac{dx_{\perp}}{dx_{||}} + \mathbf{k} \frac{dF}{dx_{||}} \right), \quad (30)$$

where the parameters  $x_j$  change within the range from 0 to  $x_{j_c}$  ( $j = ||, \perp$ ); at the given dependence  $x_{\perp} = x_{\perp}(x_{||})$   $s$  is the length of the part of the trajectory on the surface from a certain fixed point to the given one;  $\xi = dx_{||}/ds = [1 + (dx_{\perp}/dx_{||})^2 + (dF/dx_{||})^2]^{1/2}$ .

The curve  $DA$  (Fig. 1) is described by the radius-vector (29) at  $x_{\parallel} = 1 - x_{\perp}^2 g^{-2}$   $(1 - 2x_{\perp} g^{-2})^{-1}$ ,  $F = (1 - 2x_{\perp} g^{-2}) e^{-x_{\parallel}}$ . At  $g^2 \gg 1$  this curve turns into the nearly plane parabola  $F(x_{\perp}) = (1 - 2x_{\perp} g^2 + x_{\perp}^2 g^{-2}) e^{-1}$  located on the surface  $x_{\parallel} = 1 - x_{\perp}^2 g^{-2}$  perpendicular to the plane  $x_{\parallel} \propto x_{\perp}$ .

At the values  $x_{\parallel}^B = 1 - x_{\perp}^B (1 - x_{\perp}^B g^{-2})^{-1}$ ,  $x_{\perp}^B = 1 - g^2/4 - (1 - g^4/4)^{1/2}$  the curve has a minimum corresponding to the saddle-point of the surface with which the existence of the virial well is bound. At  $g^2 \gg 1$   $x_{\parallel}^B = x_{\perp}^B = 1$ ,  $F^B = e^{-1}(1 - g^{-2})$ . Here and henceforth

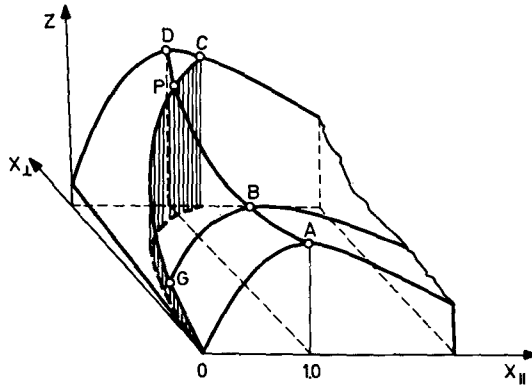


Fig. 1. Virial surface of the square lattice ( $z = F(x_{\parallel}, x_{\perp})/2D$ )

alphabetical symbols corresponding to the points on the virial surface are used as indices.

Putting  $x_{\perp} = 0$  into (29) we get the virial for a square lattice with longitudinal displacements. It completely coincides with the virial for the one-dimensional lattice with the interaction between the nearest particles each having one degree of freedom along the crystalline axis. The evolution trajectory of the system is a plane curve — it is the part  $OA$  of the virial where the point  $A = x_{\parallel}^A = 1$ ,  $x_{\perp}^A \equiv 0$ ,  $F^A = e^{-1}$  corresponds to the maximum of the virial over which the radius-vector moves as the temperature changes. The vector  $\tau$  determined by relation (30) is directed to the virial increase over the whole curve except point  $A$ . At point  $A$  the situation is changed and vector  $\tau$  takes the direction of the virial slope.

At  $x_A \neq 0$  the evolution trajectory of the lattice state is the part of the curve of the intersection of the virial surface  $F(x_{\parallel}, x_{\perp})$  and the surface corresponding to the coupling equation  $x_{\perp} = f(x_{\parallel})$ . Vector  $\tau$  has positive components for points of the latter surface and it indicates that the system has a tendency to change state with increasing temperature.



### 5. Importance of longitudinal and transversal displacements of particles in the formation of the structural instability

In Fig. 2 the temperature dependence of the functions  $x_{||}$  and  $x_{\perp}$  for different values of  $g$  are shown. From the Figure it is clear that  $x_{||}$  and  $x_{\perp}$  are less dependent on the temperature in systems where the potential is of more long range order. For the

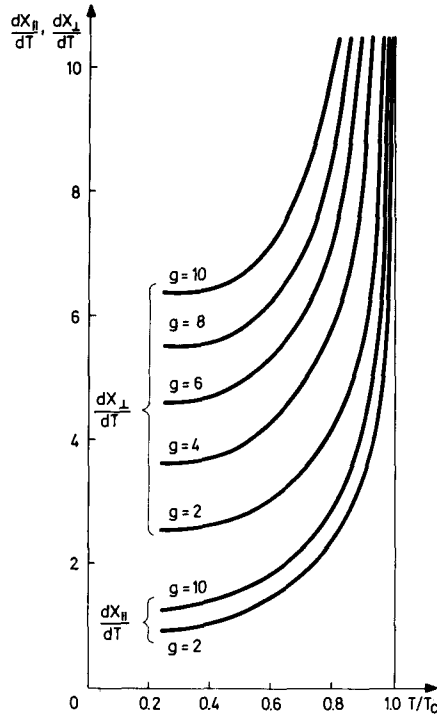


Fig. 2. Dependence of the correlation functions of the displacements  $x_{||}$  and  $x_{\perp}$  on  $T/T_c$  at different values of parameter  $g$ . The dotted line is the range of  $x_{||}$ - and  $x_{\perp}$ -values located beyond the hump of the virial surface

fixed value of  $g$  the range of change of  $x_{\perp}$  exceeds significantly that of  $x_{||}$  and the inequality

$$S_g = \frac{x_{\perp}}{x_{||}} = \frac{1}{3} \left( 1 + \frac{8}{\pi^2} \right) + \left( \frac{2}{\pi} g \right)^{2/3} x_{||}^{-1/3} > 1 \quad (31)$$

is fulfilled at any temperature  $T \leq T_c$ .

From Fig. 2 and inequality (31) it follows that the  $x_{\perp}$ -oscillations are more developed than the  $x_{||}$ -ones in the high temperature range of the crystalline state. This is also confirmed by the fact that the growth rate of the  $x_{\perp}$ -fluctuations exceeds the corresponding growth rate of  $x_{||}$ -fluctuations as temperature increases.

Differentiating Eqs. (25) and (23) with respect to temperature we get

$$\frac{dx_{||}}{dT} = \frac{k}{2D} \left( \frac{dF}{dx_{||}} \right)^{-1} \quad (32)$$

$$\frac{dx_{\perp}}{dT} = \frac{k}{2D} \left[ \frac{1}{3} \left( 1 + \frac{8}{\pi^2} \right) + \frac{2}{3} \left( \frac{2}{\pi} g \right)^{2/3} x_{||}^{-1/3} \right] \left( \frac{dF}{dx_{||}} \right)^{-1}.$$

Since at  $T_c$  Eq. (26) is fulfilled identically, then from (32) it follows that at  $T \rightarrow T_c$   $dx_{||}/dT$ ,  $dx_{\perp}/dT \rightarrow \infty$ . Hence, the approach to the instability point is accompanied by the sharp growth of the  $x_{||}$ - and  $x_{\perp}$ -fluctuations of the displacement or particles from the equilibrium position. The instability of the lattice is due not to one vibrational movement but to  $x_{||}$ - and  $x_{\perp}$ -oscillations simultaneously. However, each of them plays a different role in instability formation.

To substantiate the latter statement we consider the temperature dependences of the force constants  $\Phi_{||}$  and  $\Phi_{\perp}$  (Fig. 3) obtained on the basis of relations (19) and (20). According to Fig. 3a,  $\Phi(T)$  is a decreasing monotonic function of the temperature. Such a dependence is due to both  $x_{\perp}$  and  $x_{||}$  leading to a decrease in the value of  $\Phi_{||}(T)$  as the temperature increases. The  $x_{||}$ -correlation functions give the main contribution to the process of the lattice softening over the longitudinal force constant.

The dependence  $\Phi_{\perp}(T)$  shown in Fig. 3b differs essentially from  $\Phi_{||}(T)$ . As the temperature increases the growth of  $\Phi_{\perp}(T)$  occurs first, then this function reaches its maximum value and starts decreasing in the pre-transitional range. It follows from Eq. (20) that such behaviour of the function  $\Phi_{\perp}(T)$  is linked with the temperature competition of the stabilization and destabilization processes due to the temperature evolution of the  $x_{||}$  and  $x_{\perp}$  correlation functions.  $x_{||}$  correlation functions give a destabilizing contribution both to the longitudinal and transversal force constants.

Preliminary calculations show that the functions  $\Phi_j(T)$  for simple cubic crystals are similar to those shown in Fig. 3. According to [13] the relation between the elastic modulations  $c_{ijkl}$  and the force constants of the lattice is determined by the relations

$$\tilde{c}_{ijkl} = \frac{1}{l^3} \sum_{\mathbf{n}} \Phi_{0\mathbf{n}}^{ij} n_k n_l,$$

$$2\tilde{c}_{ijkl} = c_{ikjl} + c_{iljk}.$$

For the cubic crystals we have

$$c_{11} = \frac{c_{iii}}{2D\alpha^2} = \frac{\Phi_{||}}{l}; \quad c_{12} = \frac{c_{iij}}{2D\alpha^2} = \frac{\Phi_{\perp}}{l}.$$

Specifically, these equations allow one to interpret the anomalous growth of  $c_{12}$  and the sign change of the derivative  $dc_{12}/dT$  [20]. We note that in cubic structures of NaCl type the elastic moduli change with the temperature in accordance with the dependences obtained above [21].

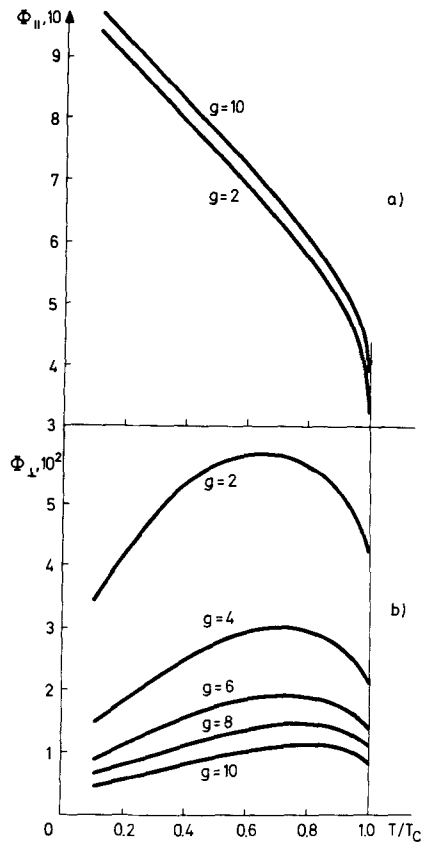


Fig. 3. Dependence of (a) longitudinal and (b) transversal force constants of the square lattice on the given temperature  $T/T_c$  at different values of parameter  $g$

Let us consider the mechanism of the formation of the system instability more thoroughly. We write the infinitesimal change of the kinetic energy of the degree of freedom and of the virial in the form

$$KdT = dF = dF_{x_{||}} + dF_{x_{\perp}}$$

where

$$dF_{x_{||}} = \frac{\partial F}{\partial x_{||}} dx_{||}, \quad dF_{x_{\perp}} = \frac{\partial F}{\partial x_{\perp}} dx_{\perp}.$$

Since  $F(x_{||}, x_{\perp})$  is a function of  $x_{\perp}$  that increases monotonically up to point  $C$  on the virial surface, then  $dF_{x_{\perp}} > 0$  over the whole of the evolution trajectory. The second differential  $d^2F_{x_{||}}$  is positive up to the crossing point  $P$  only. It changes its sign at  $P$  so the  $x_{\perp}$ -subsystem accepts the thermal energy at any point of the evolution trajectory up to the instability point, and the  $x_{||}$ -subsystem up to point  $P$  only. Beyond this, the  $x_{||}$ -subsystem transfers a part of its energy to the  $x_{\perp}$ -subsystem — which also accepts the

thermal energy from the thermostat in this range of the evolution trajectory since  $dF > 0$ . The condition  $dF_{x_{||}} = -dF_{x_{\perp}}$  corresponds to the extremum of the evolution trajectory which is reached at temperature  $T_c$ . At this temperature the increase in the kinetic energy of the lattice does not occur since due to the latter equality the  $x_{\perp}$ -subsystem is not able to accept the thermal energy of the thermostat which has already been used for the destruction of the lattice  $\left(\frac{dE}{dT} = \frac{dK}{dT} + \frac{dU}{dT} \rightarrow \infty, \text{ at } T \rightarrow T_c; E \text{ is the internal energy}\right)$ . Further temperature increase is not possible without structural change of the system because the  $x_{||}$ -subsystem is not able to transfer to the  $x_{\perp}$ -subsystem the energy excess destroying it ( $dF_{x_{||}} > dF_{x_{\perp}}$ ).

Thus, the existence of the crystalline lattice derives from the presence of the connection between the  $x_{||}$  and  $x_{\perp}$  subsystem at  $T > T_p$  and the re-distribution of the kinetic energy in this temperature range. The instability of the lattice relative to the longitudinal oscillations of particles due to the limitation of the energy capacity of the  $x_{||}$  subsystem and to the impossibility of the re-distribution of the kinetic energy between the  $x_{||}$  and  $x_{\perp}$  subsystems at  $T > T_c$  is the main cause of its structural rearrangement.

## 6. Conclusion

The first approach to the study of the structural instability of a crystal was outlined on the basis of the virial theorem of statistical mechanics in [1]. This approach is general enough. If the virial of the system could be calculated exactly merely for a certain type of interaction, then it would indicate an exact solution of the problem of the phase transition. The difficulty is that, as in the case of any other approach, the calculation of the virial relations can be carried out in certain approximations only. Therefore, the application of the pseudo-harmonic approximation to the analysis of the stability conditions, i.e. a certain procedure of the uncoupling of the multidimensional correlation functions of displacements, is not a matter of principle in qualitative considerations. Without restriction of the generality, it allows us to write a virial of the system in the real analytical form and to determine a complete set of the correlation functions describing a crystal in this approximation. Each of these correlation functions can be calculated by the use of the spectral theorem. Such a procedure allows one to add a system of virial equations up to the closed one for any number of variables in the system. The virial relations are valid for any aggregated substance since suppositions about the structural arrangement of the neighbours are not used in their derivation. But they undergo a destruction of the change type at the boundary of the temperature range of the existence of the given state. The latter is due to statistical averaging which accounts for the main structural-dynamic peculiarities of a state investigated in the description of the system with the given arrangement of particles.

In principle, due to its generality, the virial theorem allows one to describe not only an old state but also a new one arising beyond the point of the structural instability, and to build up a multiphase theorem. On its basis the model ideas about the microscopic mechanisms of the phase transitions for systems with different interatomic interaction can be consistently developed. Up-to-date achievements in the application of the virial equation of state to the interpretation of experimental data from the point of view of the interatomic interactions for macromolecules, polymers and dense gases [3, 22] suggest that the virial approach may be utilized for investigating the properties of different states of a substance including a crystalline one.

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