Influence of Strong Anharmonicity on the Dynamical Properties of a Crystal with BCC Lattice

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The correlative method of unsymmetrized self-consistent field (CUSF) is used to study dynamical characteristics of a strongly anharmonic crystal with body-centered cubic lattice, namely, the inter-atomic and mean square relative displacements. We present the general formulae for crystals with anharmonicity, including the strong one, up to fourth anharmonic terms. Taking into account the second order of the method we calculate correlations in this lattice between the nearest, second, third, fourth and fifth neighbors. The influence of more distant interactions is discussed. The results are compared with those obtained previously for an weakly anharmonic BCC crystal. We use the Schiff potencial for Na and also Lennard-Jones potentials for comparison.

I   Introduction

The quadratic correlation moments of atomic positions (QCM) as well as their mean square relative displacements (MSRD) expressing the effective amplitude of the atomic vibrations are the most important features of lattice dynamics [1, 2].

Using the dynamical theory of crystal lattice, QCM and MSRD have been calculated in the harmonic approximation [2]. However, this approximation is not more valid at high temperatures due to anharmonic effects which are of considerable importance. Here the correlative method of unsymmetrized self-consistent field (CUSF) [3, 4, 5, 6, 7, 8] is used to study the influence of anharmonic effects on the QCM and MSRD [9, 10], including strongly anharmonic ones. The general expressions for QCM and MSRD are presented taking into account anharmonic terms up to the fourth order. Recently, they have been applied to weakly anharmonic crystal with face- and body centered cubic lattices [11, 12] and also to strongly anharmonic FCC crystal [13]. In the present paper we study a strongly anharmonic BCC crystal, namely solid Na.

II   General Relations

In CUSF, the mean square relative displacements between two atoms i and j in a crystal, can be written as

$$D_{aa}(ij) = \overline{(q_{ia} - q_{ja})^2} = \overline{q_{ia}^2} + \overline{q_{ja}^2} - 2C_{aa}(ij) \; , \tag{1}$$

where a denotes the Cartesian components of atomic displacements and $C_{aa}(ij) = \overline{q_{ia}q_{ja}}$ is the correlation moment. We consider a perfect crystal with pairwise central interactions

$$U(\vec{r}, ..., \vec{r}_N) = \frac{1}{2} \sum_{i \neq j} \Phi(|\vec{r}_i - \vec{r}_j|) \; . \tag{2}$$

In this case, taking into account anharmonic terms up to the fourth order we have for variances of the atomic positions [10]

$$
\begin{aligned}
\overline{q_{ia}^2} \;=\; & \overline{a_i^2}^0 + \frac{1}{2\Theta^2}\sum_k \{\Phi_{\alpha\beta}(ik)\Phi_{\gamma\delta}(ik)\overline{\beta_k\delta_k}^0(\overline{a_i^2\alpha_i\gamma_i}^0 - \overline{a_i^2}^0\,\overline{\alpha_i\gamma_i}^0) + \\
& + \frac{1}{4}\Phi_{\alpha\beta\gamma}(ik)\Phi_{\delta\varepsilon\xi}(ik)[\overline{\gamma_k\xi_k}^0(\overline{a_i^2\alpha_i\beta_i\delta_i\varepsilon_i}^0 - \overline{a_i^2}^0\,\overline{\alpha_i\beta_i\delta_i\varepsilon_i}^0) - \\
& - 2\overline{\delta_i\varepsilon_i}^0\,\overline{\gamma_k\xi_k}^0(\overline{a_i^2\alpha_i\beta_i}^0 - \overline{a_i^2}^0\,\overline{\alpha_i\beta_i}^0) + \\
& + (\overline{a_i^2\alpha_i\delta_i}^0 - \overline{a_i^2}^0\,\overline{\alpha_i\delta_i}^0)(\overline{\beta_k\gamma_k\varepsilon_k\xi_k}^0 - \overline{\beta_k\gamma_k}^0\,\overline{\varepsilon_k\xi_k}^0)] + \\
& + \frac{1}{3}\Phi_{\alpha\beta}(ik)\Phi_{\gamma\delta\varepsilon\xi}(ik)[\overline{\beta_k\xi_k}^0(\overline{a_i^2\alpha_i\gamma_i\delta_i\varepsilon_i}^0 - \overline{a_i^2}^0\,\overline{\alpha_i\gamma_i\delta_i\varepsilon_i}^0) + \\
& + \overline{\beta_k\delta_k\varepsilon_k\xi_k}^0(\overline{a_i^2\alpha_i\gamma_i}^0 - \overline{a_i^2}^0\,\overline{\alpha_i\gamma_i}^0)]\} \;,
\end{aligned}
\tag{3}
$$

and for QCM [9]

$$
\begin{aligned}
C_{ab}(ij) \;=\; & \frac{1}{\Theta}\Phi_{\alpha\beta}(ij)\overline{a_i\alpha_i}^0\,\overline{b_j\beta_j}^0 + \\
& + \frac{1}{6\Theta}\Phi_{\alpha\beta\gamma\delta}(ij)(\overline{a_i\alpha_i\gamma_i\delta_i}^0\,\overline{b_j\beta_j}^0 - \overline{a_i\alpha_i}^0\,\overline{b_j\beta_j\gamma_j\delta_j}^0) + \\
& + \frac{1}{\Theta^2}\sum_k \Phi_{\alpha\gamma}(ik)\Phi_{\beta\delta}(jk)\overline{a_i\alpha_i}^0\,\overline{b_j\beta_j}^0\,\overline{\gamma_k\delta_k}^0 - \\
& - \frac{1}{4\Theta^2}\Phi_{\alpha\beta\gamma}(ij)\Phi_{\delta\varepsilon\xi}(ij)\overline{a_i\alpha_i\gamma_i\delta_i}^0\,\overline{b_j\beta_j\varepsilon_j\xi_j}^0 + \\
& + \frac{1}{4\Theta^2}\sum_k \Phi_{\alpha\beta\gamma}(ik)\Phi_{\delta\varepsilon\xi}(jk)\overline{a_i\alpha_i}^0\,\overline{b_j\delta_j}^0(\overline{\beta_k\gamma_k\varepsilon_k\xi_k}^0 - \overline{\beta_k\gamma_k}^0\,\overline{\varepsilon_k\xi_k}^0) + \\
& + \frac{1}{4\Theta^2}\Phi_{\alpha\beta\gamma}(ij)\sum_k(\Phi_{\delta\varepsilon\xi}(jk)\overline{a_i\alpha_i}^0\,\overline{b_j\beta_j\gamma_j\delta_j}^0 - \Phi_{\delta\varepsilon\xi}(ik)\overline{b_j\beta_j}^0\,\overline{a_i\alpha_i\gamma_i\delta_i}^0) - \\
& - \frac{1}{4\Theta^2}\Phi_{\alpha\beta}(ij)\Phi_{\gamma\delta\varepsilon\xi}(ij)\overline{a_i\alpha_i\gamma_i\delta_i}^0\,\overline{b_j\beta_j\varepsilon_j\xi_j}^0 + \\
& + \frac{1}{6\Theta^2}\sum_k(\Phi_{\alpha\gamma}(ik)\Phi_{\beta\delta\varepsilon\xi}(jk) + \Phi_{\beta\gamma}(jk)\Phi_{\alpha\delta\varepsilon\xi}(ik))\overline{a_i\alpha_i}^0\,\overline{b_j\beta_j}^0\,\overline{\gamma_k\delta_k\varepsilon_k\xi_k}^0 + \\
& + \frac{1}{6\Theta^2}\sum_k(\Phi_{\alpha\gamma}(ik)\Phi_{\beta\delta\varepsilon\xi}(jk)\overline{a_i\alpha_i}^0\,\overline{b_j\beta_j\delta_j\varepsilon_j}^0 + \\
& + \Phi_{\beta\gamma}(jk)\Phi_{\alpha\delta\varepsilon\xi}(ik)\overline{a_i\alpha_i\delta_i\varepsilon_i}^0\,\overline{b_j\beta_j}^0)\overline{\gamma_k\xi_k}^0 \;,
\end{aligned}
\tag{4}
$$

where $\Theta = kT$ is the absolute temperature in energy units, and

$$
\Phi_{\alpha\beta\ldots}(ik) = \frac{\partial\ldots\Phi(|\vec{r}|)}{\partial x_\alpha \partial x_{\beta\ldots}}\Big|_{\vec{r}=\hat{A}(n_i-n_k)} \;,
\tag{5}
$$

are the derivatives of the interatomic potential, and all Greek indices are dummy. Generally speaking, the summation extends over all K. For a perfect strongly anharmonic crystal of a high symmetry, the moments in the right sides are expressed as [14].

$$
\overline{q_\alpha^2}^0 = \frac{\beta}{3K_2}, \quad \overline{q_\alpha^2 q_\beta^2}^0 = (1 + 2\delta_{\alpha\beta})\left[\frac{2(3-\beta)\Theta}{5K_4} - \left(\frac{\beta\Theta}{3K_2}\right)^2\right] \;,
\tag{6}
$$

where $\beta(x)$ is the solution of the transcendental equation

$$
\beta(x) = 3x\frac{D_{-2.5}[x+5\beta/6x]}{D_{-1.5}[x+5\beta/6x]} \;,
\tag{7}
$$

in which $D(z)$ are the parabolic cylinder functions and x is dimensionless combination of the temperature and the second- and fourth-order force coefficients $x = K_2\sqrt{3/\Theta K_2}$,

$$K_2 = \frac{1}{3}\sum_{\alpha=1}^{3} K_{\alpha^2}, \ K_4 = \frac{3}{5}\sum_{\alpha,\beta=1}^{3} K_{\alpha^2\beta^2}, \tag{8}$$

where

$$K_{\alpha^l\beta^m} = \frac{\partial^{l+m}}{\partial q_\alpha^l q_\beta^m}\sum_{n\neq 0}\Phi(|q - \hat{A}n|)|_{q=0}. \tag{9}$$

Here $\hat{A}$ is the lattice matrix and n are vectors with integer components. The lattice matrix can be calculated from the equation of state. For cubic crystals with strong anharmonicity up to the fourth order under hydrostatic pressure it is of the form [4, 5]

$$P = -\frac{a}{3v}\left(\frac{1}{2}\frac{dK_0}{da} + \frac{\beta\Theta}{2K_2}\frac{dK_2}{da} + \frac{(3-\beta)}{4K_4}\frac{dK_4}{da}\right) + P^2 + P^H + P^Q, \tag{10}$$

where a is the nearest neighbor distance, $v(a)$ is the volume of the unit cell and $K_0(a)/2$ is the energy per molecule in the static lattice. Here P^2 and P^H are the corrections of perturbation theory, and P^Q is the first quantum correction.

III   Influence on the dynamical properties of strongly anharmonic BCC crystal

A spatial fragment of a strongly anharmonic crystal with body centered lattice is shown in Fig. 1. First we shall consider only the nearest neighbor interactions. In this case, we can see from formula (4) that the second-order perturbation theory enables the moments to be calculated up to the fifth neighbors, inclusive. For the second neighbors it is more convenient to use the crystallographic coordinate system. Finally, under a rotation of $\pi/4$ around the crystallographic Z-axis, we obtain correlation moments between the third neighbors.
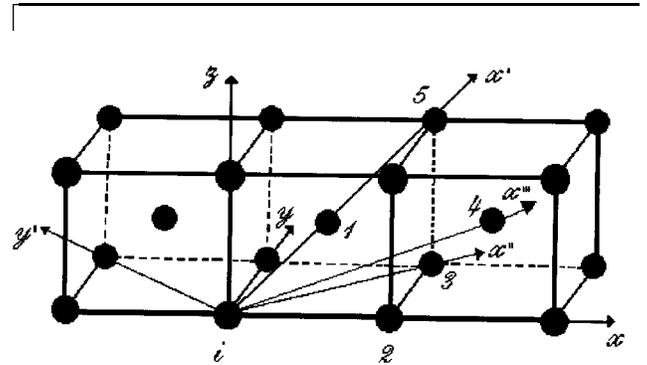
Figure 1. The arrangement of the neighbors of an atom in the BCC lattice for the spatial fragment of this lattice.

Schiff [15] proposed the following potential for sodium which is a typical crystal with the BCC lattice

$$\varphi(r)/\varepsilon = \left(A + B/R^2 + C/R^4\right)\frac{\cos(2k_F R)}{R^3} + \left(D + E/R^2\right)\frac{\sin(2k_F R)}{R^4}, \tag{11}$$

where $R = r/\sigma$, is the depth of the potential $\varepsilon/k = 599K$, $\sigma = 0.324 \ nm$ the effective diameter of an ion screened by free electrons. The parameters are: $A = 0.19$, $B = -1.02$, $C = -0.08$, $D = -0.43$, $E = -2.54$, $2k_F = 5.987$. Such potential is of an oscil-

lating form, what is known as Friedel oscillations. Essentially all calculations that use such potentials refer to numerical modelling [16].

Here we used the Schiff and the Lennard-Jones potentials for numerical evaluations. We also used the

solution the equation of state Eq. (10) obtained in reference [17]. We make this in the dimensionless form taking into account only the nearest neighbor interactions.
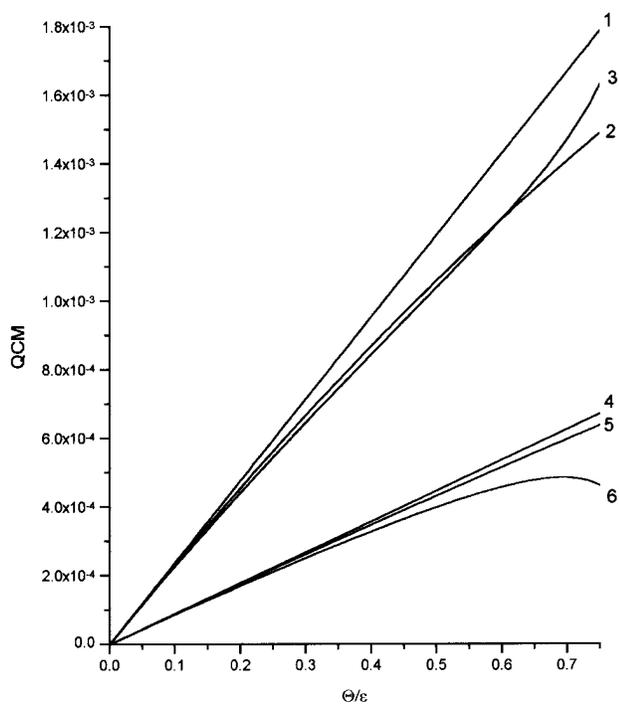
Figure 2. Quadratic correlation moments between longitudinal displacements of the nearest neighbors, $C_{xx}(1)$, calculated using various approximations: 1-harmonic, 2-weakly anharmonic, 3-strongly anharmonic, and fifth neighbors, $C_{xx}(5)$: 4-harmonic, 5-weakly anharmonic, 6-strongly anharmonic.

In Fig. 2 are plotted the correlations of longitudinal displacements between the nearest and fifth neighbors *versus* the dimensionless temperature Θ/ε for the strongly anharmonic approximation using the Schiff for Na potential, as well as the harmonic and weakly anharmonic approximations [12]. Note that at high temperatures the anharmonicity reverses the convexity of the curve $C_{xx}(1)$ and $C_{xx}(5)$ for the strongly anharmonic approximation. Moreover for this approximation $C_{xx}(1)$ becomes greater and $C_{xx}(5)$ less than the one for the weak anharmonicity.

In Figs. 3 and 4 we compare the longitudinal and transversal correlation moments respectively calculated using the Lennard-Jones and Schiff potentials. We can see that the correlation moments using the Schiff potential for Na are less anharmonic and at high temperatures their values are also less than the ones calculated

by the Lennard-Jones potential with the exception of the curves $C_{xx}(5)$ and $C_{yy}(1)$.
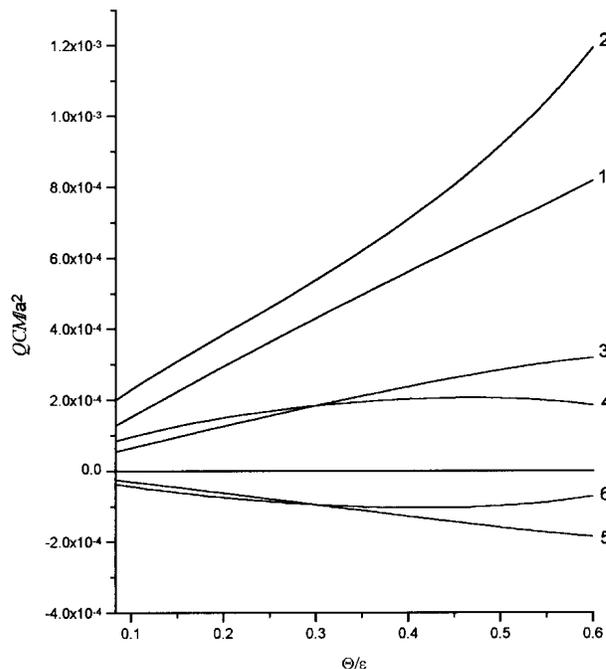
Figure 3. Longitudinal correlations moments $C_{xx}(1)$-(1,2), $C_{xx}(1)$-(3,4) and $C_{xx}(2)$-(5,6) calculated using the Schiff (1,3,5) and the Lenard-Jones (2,4,6) potentials.

The melting temperature of Na is 373 K. For temperature less than 50 K, Na has another crystal structure. For this reason we investigate the QCM and MSRD in the temperature range between 50 K and 373 K. In Fig. 5 we present the longitudinal and transversal correlations between the nearest, second, third and fifth neighbors calculated using the Schiff potential. One can see that some moments are negative implying that the corresponding atoms oscillate at such a direction for the most part opposite in phase. The negative sign of the longitudinal correlation moment in the second-order perturbation theory results from the obtuse angle between them and each of their common nearest neighbor. When this angle is acute, such a correlation is positive and in the case of straight angle, it is very small being proportional to the temperature squared. As a result of the symmetry of the coordinate systems the components of transversal correlations between the nearest, second and fifth neighbors are the same, namely $C_{yy}(n) = C_{zz}(n)$, $n = 1, 2, 5$. One can note that the transversal correlations are much smaller than the longitudinal ones.
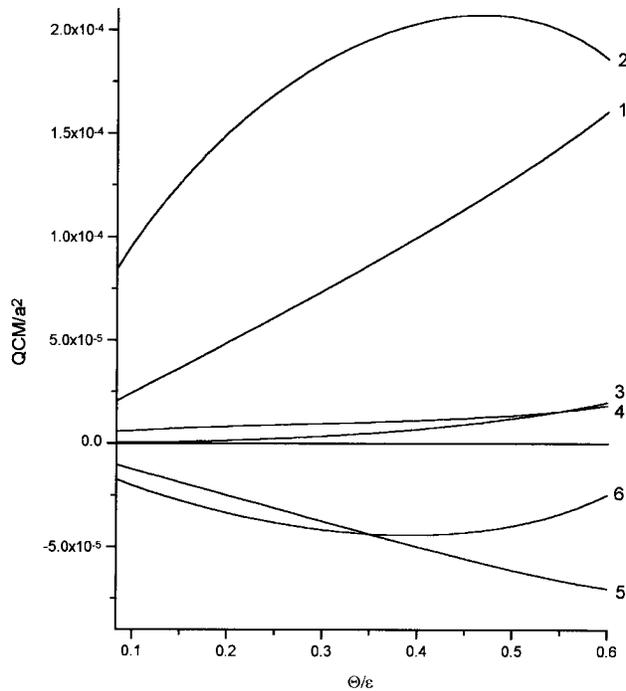
Figure 4. Transversal correlations moments $C_{yy}(2)$-(1,2), $C_{yy}(1)$-(3,4) and $C_{zz}(3)$-(5,6) calculated using the Schiff (1,3,5) and the Lenard-Jones (2,4,6) potentials.

IV An Influence of the More Distant Interactions

The interactions between more distant atoms provide the thermodynamic stability of the BCC crystal. For this reason, we shall discuss an influence of the more distant interactions on QCM for a strongly anharmonic BCC crystal. To do this we use the solution of equation of state (10) taking into account interactions up to the seventh neighbors [17].

For the BCC lattice, the difference between the nearest- and second-neighbor distances is about 15.5%, while that between the second- and third-neighbor ones is more than 40%. For this reason we include only the influence of the second-neighbor interactions on the interatomic correlations.
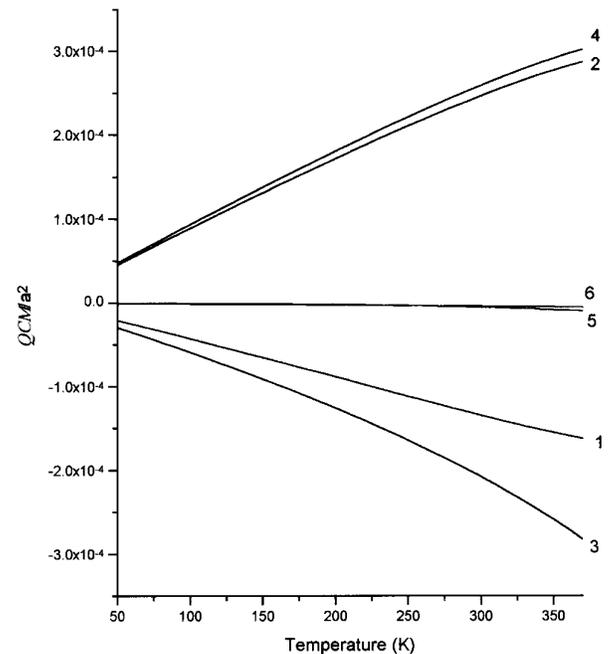
Figure 6. Longitudinal correlations moments $C_{xx}(2)$-(1,3), $C_{xx}(4)$-(5) and transversal $C_{yy}(5)$-(2,4), $C_{yy}(4)$-(6) without (1,2) and with the second-neighbor interactions (3,4,5,6), calculated using the Schiff for Na potential.

Figure 5. Correlations moments in the BCC lattice calculated using the Schiff for Na potential: $1-C_{xx}(1)$, $2-C_{xx}(5)$, $3-C_{xx}(3)$, $4-C_{yy}(2)$, $5-C_{yy}(5)$, $6-C_{yy}(5)$, $1-C_{zz}(3)$, $1-C_{xx}(2)$.

The Fig. 6 shows that an influence of more distant interactions on the correlation moments only between the second, fourth and the fifth neighbors is significant. The absolute values for both correlation moments are greater than the ones calculated without considering the contributions from more distant interactions. One notes that the correlation between the fourth neighbors is nearly zero even considering more distant neigh-

bors. The correlations $C_{xx}(4)$ and $C_{yy}(4)$ are a consequence of the interactions between the second neighbors. The correlations between the fourth neighbors are very small.

In Fig. 7 we show the mean square relative atomic displacements in the BCC crystal with strong anharmonicity calculated using the Schiff for Na potential and considering the influence of more distant interactions.
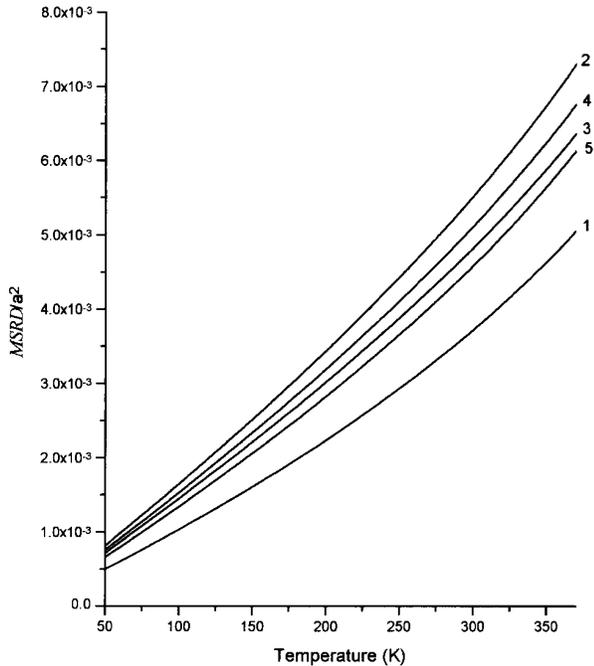
Figure 7. Longitudinal mean square relative displacemets: $1 - D_{xx}(1)$, $2 - D_{xx}(2)$, $3 - D_{xx}(3)$, $4 - D_{xx}(4) \simeq D_{xx}(n)$, $n \geq 6$, $5 - D_{xx}(5)$.

V   Conclusions

Using CUSF we have studied the interatomic quadratic correlation moments and the mean square relative displacement of atoms in a BCC crystal, namely, in solid Na at normal pressure. We evaluated the harmonic, weak and strong anharmonicity. The comparisons of theses three approximations show the importance of the anharmonic effects at high temperature.

The fact that the transversal correlations through Y and Z-axis are much smaller than the longitudinal correlations through the -axis is because you have chosen the coordinate system with X-axis running through the centers of atoms.

The negative correlations are due to the moviment of their atoms that oscillate opposite in phase.

The longitudianal correlations between the nearest neighbors in BCC lattice are greater than in FCC lattice. However, in BCC crystal the transversal correlations between the second neighbors are less than in FCC lattice.

The present work completes a series of investigations on interatomic correlations and relative displacements of atoms in low-dimensional models of anharmonic crystals [9, 10, 18] as well as in three-dimensional strongly and weakly anharmonic crystals [11, 12, 13, 19].

Finally, we used the results obtained here to study the influence of the strong anharmonicity on Lindemann's melting law which is a subject that has displayed an active interest up to the present [20].

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