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## **Fluctuations of kinetic energy at molecular dynamics and the atomic interactions in crystals**

**Key words:** interatomic interactions, molecular dynamics, silicon, phonon relaxation time

### **1. Introduction**

The molecular dynamics (MD) is a powerful method for the computer simulations of many physical and chemical properties of materials depending on temperature [1]. For example, the phenomena of thermal conductivity and structural phase transitions in solids may be studied using MD [2 - 5].

What is obtained from a molecular dynamics simulation, is the configuration or microstate of the system (the positions and momenta of every single atom) at any given time included in the simulation – a quantity that can not be measured experimentally. How to relate the microscopic configuration to macroscopic quantities that can be measured experimentally (observables), such as temperature (1) is the subject of statistical mechanics [6].

$$\langle E_k \rangle = \frac{1}{2} f k_B T , \quad (1)$$

here  $E_k$  is the kinetic energy and  $f = 3N - 3$  is the degrees of freedoms for the system (crystal) with  $N$  atoms.

Statistical mechanics is concerned with statistical *ensembles*, an ensemble being a theoretical construct holding a large number of copies (sometimes infinitely many) of essentially the same system, that is; a collection of systems described by the same set of microscopic interactions, and sharing a common set of macroscopic control variables like internal energy  $E$ , volume  $V$  and number of atoms (or moles)  $N$ . [7]

From the known Maxwell-Boltzmann distribution for kinetic energies one can obtain the relations for the relative variance in single-particle kinetic energy  $\varepsilon_k = 1/2m_k v^2$ ,

$$\frac{\Delta \varepsilon_k^2}{\langle \varepsilon_k \rangle^2} = \frac{\langle \varepsilon_k^2 \rangle - \langle \varepsilon_k \rangle^2}{\langle \varepsilon_k \rangle^2} = \frac{\langle v_k^4 \rangle - \langle v_k^2 \rangle^2}{\langle v_k^2 \rangle^2} = \frac{2}{3}, \quad (2)$$

and the relative variance in instantaneous temperature  $T$  or  $N$ -particle kinetic energy  $E_k$  [8],

$$\frac{\Delta T^2}{\langle T \rangle^2} = \frac{\Delta E_k^2}{\langle E_k \rangle^2} = \frac{2}{f} = \frac{2}{3N-3}. \quad (3)$$

Here the values  $\Delta T$  and  $\Delta E_k$  are correspondingly the standard deviations of  $T$  and  $E_k$ .

For the case of absence the limitation of the degrees of freedom the value  $f$  should be equal to  $3N - 3$  [8]. However interactions between atoms in solids may lead to the decrease of the effective value of  $f$  and consequently the value  $\Delta E_k / \langle E_k \rangle$  (3). Such an interaction may be manifested in the form of correlation the positions and velocities of neighboring atoms, which may be temperature dependent. In the latter case one may expect, for example, the temperature dependent phonon relaxation time, phonon mean free path and as a result the coefficient of thermal conductivity.

The other example of the probable change the mentioned above value of  $f$  could be the temperature stimulated structural phase transition in solids. In this case, one may expect more or less large change with temperature of the  $f$  value near the temperature of phase transition of a crystal.

In the present study, the original approach based on the study of the temperature fluctuations of the crystal's kinetic energy  $E_k$  during MD simulation has been proposed and the results of the corresponding studies are analyzed.

## 2. Method of calculations

The equilibrium-type *ab initio* MD calculations of crystals have been performed in the framework of the density functional theory (DFT) using the VASP package

[9]. The projector augmented-wave (PAW) method with a cutoff energy of 400 eV for the plane waves was employed [9, 10] together with the corresponding pseudopotentials. For the exchange and correlation terms, the gradient corrected Perdew-Burke-Ernzerhof (PBE) functional was used. The MD calculations of silicon crystals were performed at the macro-canonical NVE ensemble for different temperatures at the optimized crystal structure of the super cell  $3 \times 3 \times 3$ . Most results of MD calculations have been obtained for the simulation time up to 15 ps with the time steps of 1.5 fs. For the post MD analysis the nMoldyn 3.0 program was used [11]. In the case of  $(C_3N_2H_5)_2SbF_5$  crystals, the MD calculations have been performed at the NVT ensemble using the smaller time steps of 0.5 fs, what is caused by the light hydrogen atoms.

### 3. Results and discussion

One of the values being calculated using the results of MD is the velocity autocorrelation functions (VACF)  $C_{vv}(t)$ ,

$$C_{vv}(t) = \frac{1}{3N} \sum_{\alpha=1}^N w_{\alpha} \langle v_{\alpha}(0) \cdot v_{\alpha}(t) \rangle, \quad (4)$$

where,  $\langle v_{\alpha}(0) \cdot v_{\alpha}(t) \rangle$  denotes the averaged value of the scalar products  $v_{\alpha}(0) \cdot v_{\alpha}(t)$  for atom velocities for ion of the  $\alpha$ -type,  $w_{\alpha}$  is the weight coefficient,  $t$  the time and  $N$  the number of atoms in a supercell [11]. Due to the relatively strong bonding between atoms in solids the corresponding relatively strong correlation of atomic velocities is expected. But, on the other hand, due to the statistical character of atomic parameters and finite acoustic velocity in solids at finite temperatures the VACF is a decreasing function of a time. The latter property is manifested by the value of the VACF relaxation time  $\tau$ . The value of  $\tau$  may be compared with the mean phonon relaxation time  $\tau_{ph}$ , which is responsible for the value of coefficients of thermal conductivity  $\kappa$  and thermal diffusivity  $D$  of materials in the kinetic theory of heat conductivity [12].

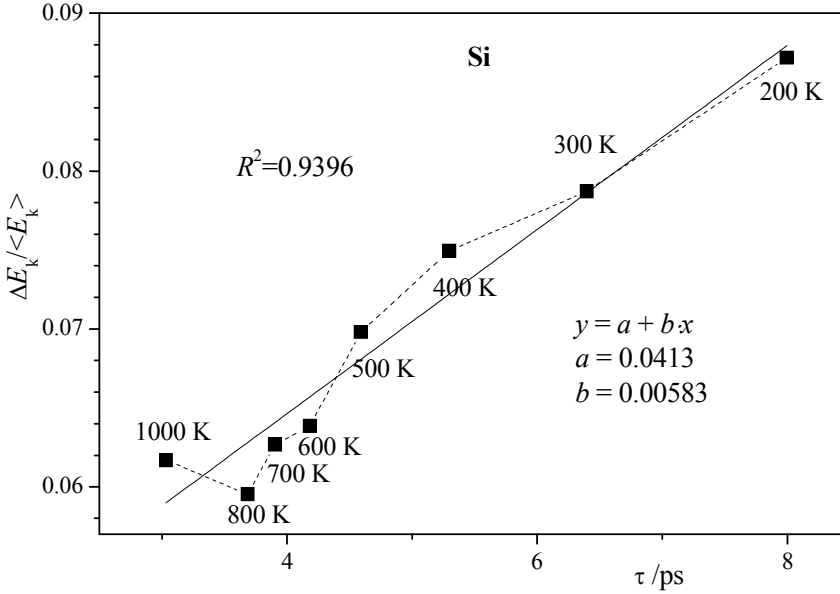
$$\kappa = \frac{1}{3} \rho C_V v^2 \tau_{ph}, \quad (5)$$

$$D = \frac{1}{3} v^2 \tau_{ph}. \quad (6)$$

where  $\rho$  is density of a material,  $C_V$  is the specific heat at constant volume  $V$  and  $v$  is the mean acoustic phonon velocity.

To verify the validity of our supposition, that due to the interatomic correlations the temperature dependence of the VACF relaxation time  $\tau(T)$  and the relative temperature changes of the kinetic energy  $\Delta E_k / \langle E_k \rangle (T)$  are dependent one from

another, we have performed the MD calculations for the silicon crystal at different temperatures in the range of 200 K - 1000 K. The MD calculations within the NVE ensemble were performed for the silicon supercell  $3 \times 3 \times 3$  containing 216 atoms. The fitted linear dependence with the coefficient of determination (COD)  $R^2 \approx 0.94$  between the values  $\tau$  and  $\Delta E_k / \langle E_k \rangle$  indicates for the relatively high degree of correlation between these values (Fig. 1).



**Fig. 1.** Correspondence between the VACF relaxation time  $\tau$  and the relative change of kinetic energy  $\Delta E_k / \langle E_k \rangle$  of silicon obtained on the basis of MD calculations at different temperatures in the range of 200 K - 1000 K

The linear fit,  $y = a + b \cdot x$ , of the dependence between the values  $\Delta E_k / \langle E_k \rangle$  and  $\tau$  is characterized by the relatively high coefficient of determination  $R^2 = 0.9296$  (Fig. 1), that is a clear proof for the validity of this relation. Here  $\Delta E_k$  is the standard deviation of the kinetic energy  $E_k$  and  $\langle E_k \rangle$  is the averaged value of kinetic energy. This relation could be useful for estimation the temperature dependent mean phonon relaxation time  $\tau_{ph}$  and the coefficient of phonon thermal diffusivity  $D$  of silicon by means of calculation the value of  $\Delta E_k / \langle E_k \rangle$ . Of course, the fitting parameters  $a$  and  $b$  found (Fig. 1) are characteristic for silicon. Due to the straightforward calculation of the value  $\Delta E_k / \langle E_k \rangle$  on the basis of the molecular dynamics run the proposed approach may be applied also for study of the coefficient of phonon thermal diffusivity  $D$  and thermal conductivity  $\kappa_{ph}$  as functions of different factors: chemical composition, temperature, pressure, etc.

## Conclusions

1. The relative fluctuations of the silicon crystal kinetic energy  $\Delta E_k / \langle E_k \rangle$  have been found to be in the inverse dependence with the temperature.
2. Clear correlation with the relatively high coefficient of determination  $R^2 = 0.9296$  has been revealed between the fluctuations of the silicon crystal kinetic energy  $\Delta E_k / \langle E_k \rangle$  and the corresponding relaxation time  $\tau$  of the velocity autocorrelation function and the phonon relaxation time. This substantiate the use of the proposed approach for the calculation of values related to the heat conductivity in the silicon based semiconductors.

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## **Abstract**

The calculation method of the molecular dynamics has been applied to study the correlation of the kinetic energy fluctuations and the relaxation time of the velocity autocorrelation function and the phonon relaxation time in a crystal. On the basis of the molecular dynamics data for silicon crystal obtained at different temperatures in the range 200 K – 1000 K the correlation between the kinetic energy fluctuations and the relaxation time of the velocity autocorrelation function has been calculated with the relatively high coefficient of determination  $R^2 = 0.9396$ . The correlation obtained and the corresponding approach substantiate a use of the kinetic energy fluctuations for the calculation of values related to the heat conductivity in the silicon based semiconductors (coefficients of thermal conductivity and diffusivity).

## **Streszczenie**

Obliczeniowa metoda dynamiki molekularnej została zastosowana do badania korelacji fluktuacji energii kinetycznej i czasu relaksacji autokorelacyjnej funkcji prędkości i czasu relaksacji fononów w kryształach. Na bazie danych dynamiki molekularnej kryształu krzemu otrzymanych w różnych temperaturach w zakresie 200 K – 1000 K została obliczona korelacja fluktuacji energii kinetycznej i czasu relaksacji autokorelacyjnej funkcji prędkości, która cechuje się stosunkowo wysokim współczynnikiem determinacji  $R^2 = 0.9396$ . Otrzymana korelacja uzasadnia zastosowanie fluktuacji energii kinetycznej do badań obliczeniowych wielkości powiązanych z przewodnością cieplną półprzewodników na bazie krzemu (współczynniki przewodności i dyfuzyjności cieplnej).

**Słowa kluczowe:** oddziaływania międzyatomowe, dynamika molekularna, krzem, czas relaksacji fononów