A method for treating thermal expansion effects in molecular dynamics simulations for solids

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Abstract. We report a simple and efficient method for including thermal expansion at high temperatures for solids in molecular dynamics simulations. The method is based on the application of the bulk modulus and the virial theorem for internal microscopic stress to allow a system to expand for a desired temperature. With appropriate scaling, zero-external-pressure conditions can be achieved rapidly. We also discuss techniques developed in this work for establishing thermal equilibrium of a solid at various temperatures, including the use of the equipartition-of-energy theorem as a criterion at low temperatures. The results of molecular dynamics simulations show good agreement with the experimental data for rare gas and ionic crystals.

1. Introduction

For many years, molecular dynamics (MD) simulations have been widely used to study various properties of solids and liquids [1, 2]. By this method, one can investigate macroscopic properties in terms of microscopic picture of atomic motion in a system. For example, one of the MD calculations is to study ionic diffusion in superionic conductors [3]. This simulation method has also been applied to study thermal conduction in solids as well as ejection mechanisms of energetic particle bombarded semiconductors and metals [4, 5]. Furthermore, MD calculations are employed to study melting phenomena in solids [6].

In many cases, achieving thermal equilibrium for solids is the first step to obtain a well behaved system with the correct thermal properties such as average temperature, kinetic and potential energy, and pressure. In particular, quantitative confirmation of such a thermal equilibrium state in MD calculations has been ignored [7]. In practice, a computer simulation often starts with a uniform velocity distribution for atoms in the solids, and no initial vibrational displacements are included. From these unrealistic initial conditions, the system has to be allowed to run for several thousand time steps for thermalization to occur [7].

Secondly, at high temperatures, the anharmonic nature of the atomic interaction becomes more significant and leads to thermal expansion and other effects. MD calculations should take these effects into account by allowing the system to expand until zero external pressure is obtained. Neglect of these effects causes simulation results to

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deviate from experimental data. The studies of ionic motion in Ag_2S and α-AgI, have revealed that the mean square displacements of ions are smaller than those obtained from experiments [3].

Several comprehensive methods of allowing the volume to change in MD simulations have been proposed by Anderson [8] and developed by Parrinello and Rahman [9]. They introduce a dynamic h tensor in the Hamiltonian with a phenomenological parameter Ω, referred to as the extended mass. This tensor characterizes the time variation of the MD cell in size and shape in response to differences between the internal microscopic stress and external pressure. The new approach allows formulation of several different kinds of ensembles for MD calculations. Ray has discussed the microcanonical $[EVN]$ and the $[HPN]$ ensembles in detail [10, 11].

Haile and Graben have applied the new MD methods to study thermal properties of Lennard-Jones (LJ) fluid for an isoenthalpic–isobaric $[HPN]$ ensemble under hydrostatic pressure, for which the dynamic tensor h reduces to a scalar [12]. In this calculation, for a given temperature and specified external pressure, the volume of the system will automatically adjust to a correct value. The thermal expansion coefficient can be calculated from the cross fluctuation of the product of kinetic energy and volume as given by Ray *et al* [11]. An alternate method of obtaining the thermal expansion coefficient for a microcanonical ensemble developed by Ray and Graben [13] is also based on a fluctuation theory, but requires prior use of an $[HPN]$ ensemble [9].

The more sophisticated methods are useful for extensive MD calculations of thermal expansion coefficients. However, in many applications, a simple and efficient method for including thermal expansion is more desirable in terms of easy implementation in computation and at the same time treating basic physics correctly as done with the comprehensive methods mentioned above. We shall develop such a method and apply it to the cases of rare gas and ionic solids. We shall also propose to use the equipartition-of-energy theorem as a criterion for monitoring thermal equilibrium of a solid at low temperatures. At high temperatures, the deviation from energy equipartition can occur due to the anharmonic forces. Therefore, we will give a simple classic theory which allows us to calculate the amount of the deviation and compare with MD results.

2. Method

First, we use the well-known LJ potential for the atomic interaction. The strength ε and size σ parameters are taken to be for argon [14]. We shall also apply MD calculations to other rare gas solids and ionic crystal NaCl as discussed in section 3. An FCC lattice structure is used, and a leap-frog algorithm [7] is employed to solve atomic trajectories. The time step is $\Delta t = 0.05$ ps, compared to the Debye period 0.6 ps for argon. In addition, we use a cut-off distance $r_c = 2.0a$, where a is the lattice parameter. Primarily, we include 256 atoms in the computational cell and apply periodic boundary conditions in all the three directions.

Initial atomic velocities are generated by using a Monte Carlo method according to the Maxwellian distribution rather than a uniform distribution as done by Anastasiou and Fincham [7]. After preliminary values are selected for atomic velocities, corrections are applied to adjust the total linear momentum of the system to zero, and then the velocities are rescaled to obtain the desired initial temperature.

For small oscillation of atoms, we can expand the potential energy per atom into a Taylor series around the minimum as

$$\Delta U = U - U_0 = c\delta^2 - g\delta^3 - f\delta^4 - h\delta^5 \tag{1}$$

where $\delta = r_i - r_{i0}$ is the displacement from the equilibrium position of the static lattice and $c = \frac{1}{2} \, \mathrm{d} U/\mathrm{d} r^2|_{r_{i0}}$, etc. In addition, U_0 is the cohesive energy per atom of the static lattice and equal to $-8.6 \, \varepsilon$ calculated from the FCC lattice summations given by Kittel [14]. At low temperatures the harmonic term in the expansion is dominant. Therefore, we can also generate initial atomic displacements with a Maxwellian distribution, and then rescale the displacements so that $c\delta^2_{\text{RMS}} = \frac{3}{2}k_B T$. In this manner, before the MD simulation, the microscopic state of a many body system is specified by appropriate distributions, thermal equilibrium is expected to be achieved rapidly.

The pressure of the system is calculated by using the well-known virial theorem:

$$P = (2K - \Psi)/3V \tag{2}$$

where K is the kinetic energy, and V the volume of the system, and Ψ the virial. The potential energy and the virial are calculated in the same loop which is used to evaluate the forces for atoms within the cut-off distance r_c. Therefore, it is necessary to include the long range corrections to these quantities to compensate for the omitted interactions $r > r_c$. This is achieved by assuming a uniform average density of atoms at $r > r_c$. These corrections are given below for three dimensions

$$\Phi_{\text{LRC}} = \frac{N^2}{2V} \int_{r_c}^{\infty} u(r)4\pi r^2 \, \mathrm{d}r = \frac{8\pi\varepsilon N^2\sigma^2}{3V}\left[\frac{1}{3}\left(\frac{\sigma}{r_c}\right)^9 - \left(\frac{\sigma}{r_c}\right)^3\right] \tag{3.1}$$

$$\Psi_{\text{LRC}} = \frac{N^2}{2V} \int_{r_c}^{\infty} r\frac{\mathrm{d}u(r)}{\mathrm{d}r}4\pi r^2 \, \mathrm{d}r = \frac{16\pi\varepsilon N^2\sigma^2}{V}\left[\left(\frac{\alpha}{r_c}\right)^3 - \frac{2}{3}\left(\frac{\sigma}{r_c}\right)^9\right] \tag{3.2}$$

where $u(r)$ is the pair potential, r_c the cut-off distance, and N the number of atoms.

As the temperature of the system increases, atoms have more kinetic energy, vibrational displacements are larger, and the pressure of the system becomes very high for a fixed volume. But the state of the system at constant volume (fixed lattice parameter), which is convenient for computational purposes, does not correspond to the usual experimental conditions for a solid. Nevertheless, one may have other objectives like simulations along an isochore. In this work, we wish to perform MD simulations according to usual experimental situations at a constant pressure of one atmosphere, which is essentially zero in terms of any substantial compression of the solid. Hence we develop a method below to adjust the lattice parameter so that the external pressure on our model system becomes effectively zero at each temperature. Because the bulk modulus of a crystal has very weak dependence on temperature [15], we assume it to be constant and use a value of $B = 75.1 \, \varepsilon/\sigma^3$ also calculated from the static lattice summations. After integrating the bulk modulus $B = - V \, \mathrm{d}P/\mathrm{d}V$, we find the volume of the system as a function of pressure:

$$V|_{P=0} = V \exp(P/B) \tag{4}$$

where $V|_{P=0}$ is the volume at zero pressure. Since the volume is proportional to the lattice constant a, we obtain the following expression:

$$a|_{P=0} = a \exp(P/3B) \tag{5}$$

where $a|_{P=0}$ is the lattice constant at a non-zero temperature for zero pressure. Note

here $a|_{P=0}$ is not the same as the static lattice parameter a_0. The method of relaxing lattice parameters for zero external pressure is easy to be implemented in MD simulations as we will discuss its application and the results in section 3.2.

3. Discussion of results

3.1. Equipartition of kinetic and potential energy

With the initial conditions selected as described in section 2, the system is allowed to evolve for several hundred time steps (300) to reach thermal equilibrium. The criterion of establishing thermal equilibrium for the system at low temperatures is to monitor equipartition of the kinetic and potential energy. For a classical system, each degree of freedom for which the energy depends quadratically on the coordinate has an average energy $\frac{1}{2}k_B T$. Hence at low temperatures, we expect both the kinetic and potential energy per atom to be equal to $\frac{3}{2}k_B T$. The potential energy per atom is expressed in terms of the difference between the total potential energy and the cohesive energy per atom U_0 of the static lattice:

$$\Phi_{th} = \sum_{\text{pairs}} u(r) - NU_0. \tag{6}$$

We illustrate in figure 1 the results of a computer simulation for the thermal equilibration of argon solid in terms of the kinetic, potential and total energy per atom as a function of time. The total energy is also given with respect to NU_0. In figure 1(a) the desired temperature is 10 K with a lattice parameter $a = 5.26$ Å for zero external pressure. Equipartition of energy is readily observed, since the displacements of atoms around their equilibrium positions are small at this low temperature. With a small number of atoms, the root-mean-square fluctuations are about 3–5% of the thermodynamic quantities. Because of the properly chosen initial conditions, this figure shows no noticeable time lag for the partitioning of the kinetic and potential energy.

At relatively high temperatures, the anharmonic terms in the expansion of the interatomic potential in equation (1) become more noticeable. As a result, the average potential energy becomes larger than the average kinetic energy at a finite temperature. Therefore, a deviation from equipartition of kinetic and potential energy should be obtained instead of exact equipartition of energy. We show this kind of potential energy deviation for MD calculations in figure 1(b) for $T = 50$ K, which is approaching the Debye temperature ~ 81 K for argon. We can also work out a simple classical theory to compare to the MD results. By employing the Boltzmann distribution function, we expand the anharmonic terms in the exponent, as is commonly done for a similar treatment of thermal expansion [14]. The average potential energy per atom for one degree of freedom is given by

$$\Delta U = k_B T/2 + (3f/4c^2)k_B^2 T^2 = k_B T/2 + \eta T^2 \tag{7}$$

where c and f are defined in equation (1). The first term is precisely the contribution from the harmonic term of the interatomic potential and gives the theorem of equipartition of energy. The second term shows the additional contribution from the anharmonic part of the potential at high temperatures.

We have conducted a series of MD simulations for several temperatures. The MD results and comparison with the classical theory are given in table 1 for argon. The kinetic energy is also given for comparison. These results are obtained by averaging over 300
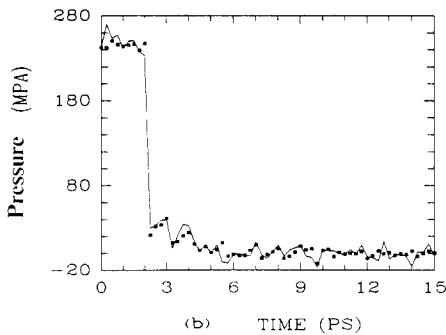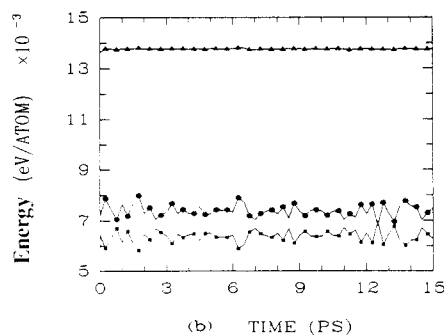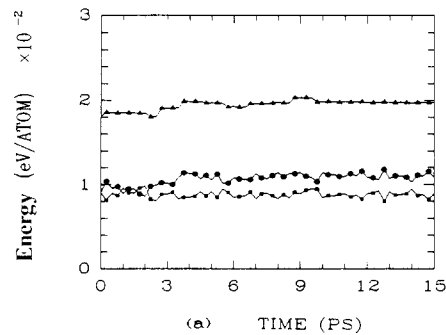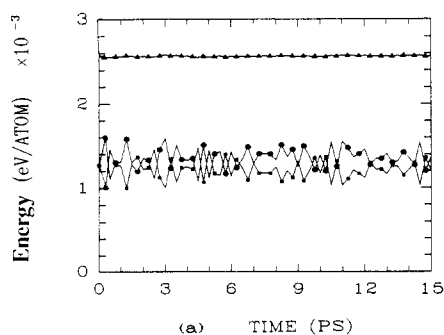
Figure 1. MD results of thermalization of argon system at (*a*) $T = 10$ K with $a = 5.26$ Å and (*b*) $T = 50$ K with $a = 5.35$ Å. The triangles, squares and circles are for total, kinetic and potential energies, respectively.

Figure 2. MD results on adjustment of lattice parameters to reduce pressure to zero for a desired temperature 70 K. (*a*) The total, kinetic and potential energies defined in figure 1 as a function of time. (*b*) The adjustment of pressure as a function of time.

Table 1. Kinetic and potential energies, and lattice parameters as a function of temperature for argon. The energies are in units of 10^{-3} eV/atom

T (K)	Kinetic energy (10^{-3} eV/atom)	Potential energy (MD results) (10^{-3} eV/atom)	Potential energy (theory) (10^{-3} eV/atom)	Lattice parameter (Å)
10	1.29	1.37 ± 0.07	1.30	5.262
20	2.58	2.79 ± 0.16	2.61	5.282
30	3.88	4.34 ± 0.32	3.93	5.305
40	5.17	5.79 ± 0.36	5.26	5.328
50	6.46	7.20 ± 0.23	6.60	5.354
60	7.76	8.84 ± 0.19	7.96	5.381
70	9.05	11.02 ± 0.31	9.32	5.412
80	10.34	11.37 ± 0.39	10.70	5.442

time steps. The root-mean-square fluctuations are relatively large because of the short runs. At 10 K, the kinetic and potential energies of MD calculations show agreement and this indicates that proper energy equipartition is achieved. At high temperatures, energy

equipartition is not satisfied as the potential energy deviates from the kinetic energy with temperatures. In the temperature region of about 20–40 K, the comparison for the potential energies between the MD results and theory the (equation (7)) shows some difference. This difference can be attributed to the fact that MD simulations actually employ the anharmonic atomic interaction whereas the theory only approximately provides some small corrections to the potential energy. As temperature increases further, the difference becomes more significant because the expansion in the simple classical theory completely breaks down.

Since at high temperatures the potential energy is larger than the kinetic energy as a result of the anharmonic characteristics of the interatomic potential, we can actually allow the system to start with sufficient potential energy for a given temperature. We shall discuss in the next section how to obtain the appropriate lattice parameter for each temperature. In practice, we first use a harmonic approximation (as discussed in section 2) to obtain initial atomic displacements and corresponding potential energy per atom Φ_h. Then we scale the atomic displacements by

$$\mathrm{d}x_i' = \sqrt{\Phi_{th}/\Phi_h}\ \mathrm{d}x_i \qquad (8)$$

where Φ_{th} is the correct amount of potential energy as given in table 1. Also $\mathrm{d}x_i$ is the x-component of the displacement for the ith atom before scaling the $\mathrm{d}x_i'$ after scaling. This method of obtaining initial atomic displacements is efficient even at higher temperatures. Figure 1(b) displays the application of this method for argon at $T = 50$ K.

The use of the equipartition-of-energy theorem allows us to have quantitative confirmation that the system reaches thermal equilibrium. We have applied the conventional method to carry out several molecular dynamics calculations with initial Maxwellian velocity distributions but no initial atomic displacements. As expected from the equipartition-of-energy theorem at low temperatures, half of the initial kinetic energy is converted to potential energy as thermalization proceeds. It is observed that the system takes about 2 to 4 ps to reach thermal equilibrium (see figure 2). To establish a desired temperature, atomic velocities must be rescaled several times. After each velocity scaling, the thermal relaxation time (2 to 4 ps) is required to allow this input of kinetic energy to partition properly with potential energy. Furthermore, at higher temperatures, the number of times for scaling increases because of larger atomic vibrations. With a uniform initial velocity distribution and no atomic displacements a system even requires a much longer time to reach thermal equilibrium [7]. It takes some time for the system to approach a Maxwellian distribution of atomic velocities, in addition to the relaxation time for partitioning of energy. Therefore, the method of introduction of initial atomic velocities and displacements with Maxwellian distributions has proven to be much more efficient for the establishment of thermal equilibrium of a many-body system.

3.2. Thermal expansion at high temperatures

In applying the lattice parameter relaxation method (see section 2) for MD simulations at high temperatures, we start with initial conditions with a desired temperature and static lattice parameter a_0 for $a(T)$. During the first 60 steps without any scaling, the pressure is very high as shown in figure 2(b) for a desired temperature 70 K. Then a is relaxed, and this sudden change of a increases the relative distances between atoms as well as the potential energy. Thus, the kinetic energy decreases. For a desired temperature, we alternatively adjust the lattice parameter a and rescale the atomic velocities at every 40 steps. Strictly speaking, adjustment of total linear momentum had
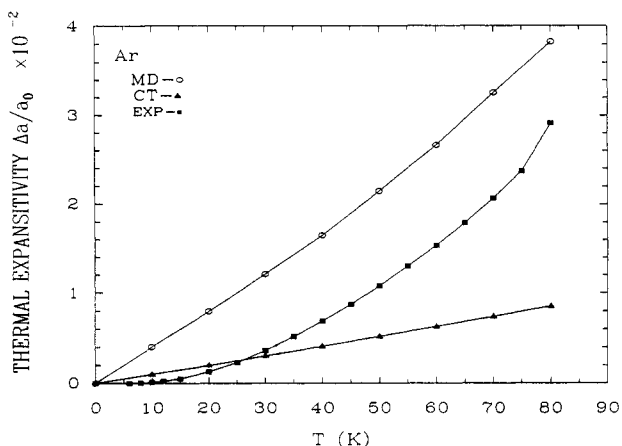
Figure 3. Thermal expansivity of argon solid as a function of temperature. CT denotes the results of a classic theory discussed in the text. a_0 is the lattice parameter at $T = 0$.

better be repeated after the adjustment, since momentum is a conserved quantity. We display the adjustments of the total, potential, and kinetic energies in figure 2(*a*). The deviation from energy equipartition at this high temperature is also evident.

With several adjustments, the pressure is reduced to zero within the fluctuations as a suitable lattice parameter is obtained as shown in figure 2(*b*). The adjustment stops at 200 steps ($t = 10$ ps), and then the system is allowed to run 100 steps ($t = 5$ ps) to reach the final thermal equilibrium. Using this method, we have performed a series of computer runs at different temperatures for argon and obtained the correctly adjusted lattice parameters given in table 1.

We show MD results compared to experimental data in figure 3 for argon. Thermal expansivity is defined as $(a(T) - a_0)/a_0$ where $a(T)$ and a_0 are lattice parameters at a finite temperature and the reference temperature, respectively. The slope of these curves gives the thermal expansion coefficient. In this case, molecular dynamics results show good agreement with experimental results [15] in the temperature region ($T \simeq 30$–70 K).

The curve denoted by CT shows the results of a classical theory of thermal expansion given by Kittel [14]. The result is obtained by averaging atomic displacements with a Boltzmann distribution. We find the average displacement δ is

$$\delta = 3gk_B T/4c^2 + 15hk_B^2 T^2/8c^3 = \alpha T + \gamma T^2 \tag{9}$$

where c, g and h are the coefficients in the expansion of the interatomic potential as defined in equation (1). Since the value of γ is very small, the quadratic term is not very evident in figure 3.

When the temperature goes to absolute zero, the expansion coefficient vanishes as shown by the experimental data. Obviously, this indicates that molecular dynamics fails at low temperatures where quantum effects become important. Nonetheless, these results do show that the MD simulations fully reveal the anharmonic effect of the interatomic potential. Consequently, at high temperatures, MD can still produce the correct expansion behaviour as compared with experiment. The method has been applied to study krypton and xenon with the appropriate ε, σ, atomic mass, and the
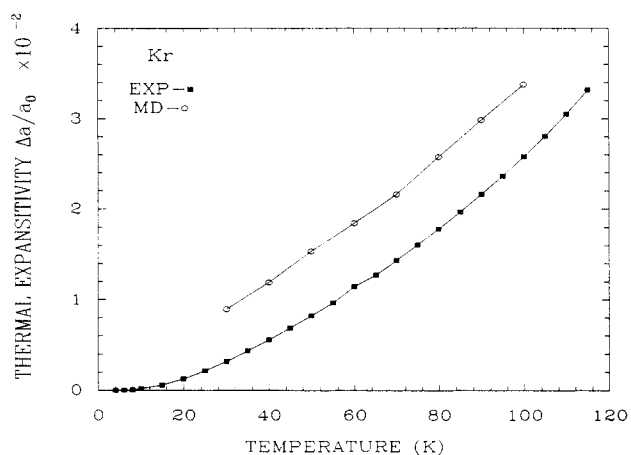
Figure 4. Thermal expansivity of krypton as a function of temperature.
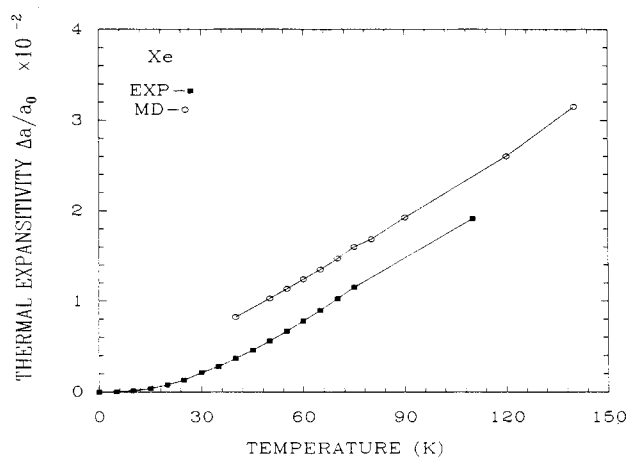

Figure 5. Thermal expansivity of xenon as a function of temperature.

simulation parameters. The MD results for krypton and xenon as shown in figures 4 and 5 demonstrates less difference from experiment as the atomic mass increase since the quantum effects are less important for the heavier atoms.

3.3. Thermal expansion in ionic crystals

Our method of relaxing the lattice parameter has proven to work properly for rare gas solids. As a further test, we have applied the method to ionic crystals such as NaCl. In this context, we included 108 sodium and chlorine ions respectively in the computational cell. For the non-Coulomb interaction, the Born–Mayer–Huggins (BMH) potential is employed [7]. The Coulomb interaction between ions is included by the means of the
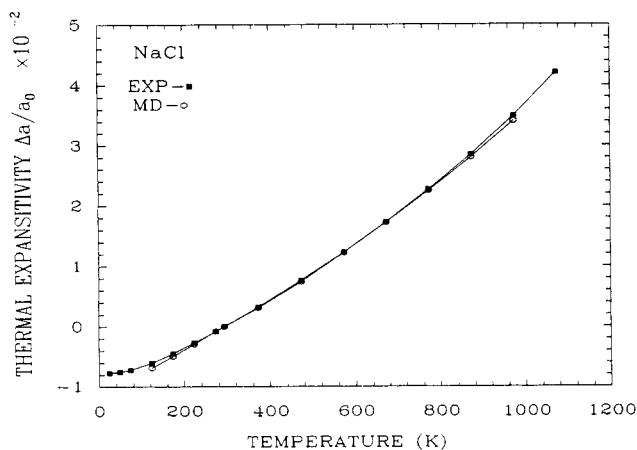
Figure 6. Thermal expansivity of a NaCl crystal as a function of temperature. a_0 is the lattice parameter at $T = 293.15$ K.

Ewald sum. Figure 6 shows thermal expansivity of NaCl at various temperatures for MD results and experiment [16]. The comparison displays an even better agreement than for the case of rare gas solids. The LJ potential has an inverse twelfth power term for the repulsive part which is very steep at short range whereas the BMH potential employs a soft exponential form (but it has scaling problems). This difference may cause the very large thermal expansivities of the LJ model as compared with experiment.

4. Conclusion

The validity of the method for including thermal expansion is clearly established as demonstrated by the results of our MD calculations and their good agreement with experiments for both rare gas and ionic crystals. This direct approach treats basic physics correctly as the sophisticated methods and thus provides an alternative way to take thermal expansion into account in an efficient manner. We also outlined a method for initializing a MD simulation close to thermal equilibrium state by using a Monte Carlo method to obtain initial atomic velocities and displacements with Maxwellian distributions. The results showed that the system reaches thermal equilibrium in a relatively short time with these realistic initial conditions. The equipartition-of-energy theorem is satisfied at low temperatures where the harmonic force dominates. Thus, it can be used as a quantitative measure for thermal equilibrium of a solid under low-temperature conditions. The deviations from energy equipartition due to the anharmonic characteristics of the atomic interaction are observed at high temperatures. The MD results for these deviations are larger than those calculated from a classic theory given in this work. The deviations can be an interesting subject for simulations with better statistics.

Acknowledgments

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