

A model for including thermal conduction in molecular dynamics simulations

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A technique is introduced for including thermal conduction in molecular dynamics simulations for solids. We develop a model to allow energy flow between the computational cell and the bulk of the solid when periodic boundary conditions cannot be used. Thermal conduction is achieved by scaling the velocities of atoms in a transitional boundary layer. The scaling factor is obtained from the thermal diffusivity, and the results show good agreement with the solution for a continuous medium at long times. We have investigated the effects of different temperature and size of the system, and of variations in strength parameter, atomic mass, and thermal diffusivity. In all cases, no significant change in simulation results has been found.

I. INTRODUCTION

Fourier's law of heat conduction has been successfully used to study thermal conduction in continuous media for many years.¹ It seems obvious to propose that the heat flux is a function of the thermodynamic state and the temperature gradient. The simplest approximation is that the heat flux is linear in the temperature gradient, and with the assumption of isotropic material we arrive at $\mathbf{J} = -\kappa \nabla T$. In this paper we shall develop a microscopic formulation to apply and test the validity of this law.

In molecular dynamics (MD) calculations of solids, periodic boundary conditions are often used to simulate an infinite system. In some cases, however, these convenient conditions cannot be applied. For example, in simulation of surface melting,² the presence of the surface eliminates the use of the vertical periodic boundary. In practice, atoms or ions at the deeper-lying layers are kept fixed to simulate the interaction between the surface region and the bulk of the solid. When heat is applied to the surface, the velocities of atoms in the surface layer are scaled to represent input of energy. But the fixed lower boundary does not allow energy flow into the bulk of the crystal, resulting in overestimation of the melting process.

The heat transfer problem also occurs in the study of the thermal relaxation in a dense liquid under shock compression.³ A dense, three-dimensional column of a simple modified Lennard-Jones liquid is simulated, shock compression is initiated by causing the column to move in the longitudinal direction with a velocity of $-U_p$. In the transverse directions, periodic boundaries are used. In this study, no thermal conducting boundaries are included in the simulation, but a scaling of kinetic energy for all atoms is artificially introduced to model thermal contact with the surrounding liquid.

Another similar example is given in a study of radiation-induced electrostatic disruption of insulator surfaces.⁴ After solids are bombarded by energetic particles, some atoms are ionized near the surface, and thus a significant amount of Coulomb potential energy is introduced into a local region of the system. Obviously, lateral periodic boundary conditions cannot realistically describe a charged insulator surface in

the molecular dynamics simulation, since an infinite amount of potential energy would be established by an infinite array of charges. Therefore, we first adopted fixed boundaries for the sides and bottom of the charged region, but, as for the case of surface melting, no energy flow is allowed by the fixed boundary. As a result, some extra energy is kept in the cell and gives rise to an unphysical characterization of dynamic behavior of the system, especially in a long time scale. In the study of atomic ejection from rare-gas solids by low-energy cascades,⁵ this effect was also ignored. Therefore, a realistic model for solving these problems should include thermal conduction from the computational cell through its boundary to the bulk of the solid.

II. MODEL FOR THERMAL CONDUCTING BOUNDARY

For the MD calculations we consider a local region of a 2D solid containing 144–400 moving atoms. The simplest nonperiodic boundary conditions are obtained with a fixed boundary, which can be provided by surrounding the computational cell with four layers of permanently fixed atoms. (A reasonable cutoff distance for the LJ potential between atoms is 4.2 atomic spacings.) In this way, the local region described by the computational cell is connected to the bulk of the solid, but unfortunately no energy transfer is possible to the fixed atoms.

In order to model thermal conduction, we further introduce a transition layer of atoms between the computational cell and the fixed boundary. Atoms in this transition layer are allowed to move, so they will interact with atoms both in the cell and in the fixed boundary. The average temperature of atoms in the transition layer is then scaled every few time steps to simulate energy flow out of the computational cell. We now proceed to obtain the scaling factor from an atomic description of thermal conduction.

According to the definition of specific heat, the amount of heat dQ entering a mass element δm for a change of temperature dT is given by

$$dQ = \delta m c dT = \delta x \delta A \rho c dT, \quad (1)$$

where c is the specific heat, δx the width of the transition layer, ρ the density of the material, and δA the unit area with

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normal direction perpendicular to the transition layer. The rate of heat change is just

$$\frac{dQ}{dt} = J \delta A, \quad (2)$$

where the energy flux J is related to the temperature gradient by

$$J = -\kappa \frac{dT}{dx}, \quad (3)$$

where κ is the thermal conductivity. With these relations we find

$$\frac{dT}{dt} = -\frac{\kappa}{\rho c \delta x} \frac{dT}{dx}, \quad (4)$$

In order to apply this method to our molecular dynamics model, we approximate dT/dx by $(T_a - T_0)/\delta x$, in which T_0 is the background temperature of the bulk solid and T_a is the temperature of the atoms in the transition layer. dT/dt is also approximated by $\delta T/\delta t$. Equation (4) can be rewritten as

$$\frac{\delta T}{\delta t} = -D \frac{T_a - T_0}{(\delta x)^2}, \quad (5)$$

where D is the thermal diffusivity $D = \kappa/\rho c$. For δt we use

$$\delta t = n \Delta t, \quad (6)$$

where Δt is the time interval for one step of the molecular dynamics calculation, and n is the number of time steps after which the velocities of the transition atoms are scaled. Then we obtain

$$\delta T = -\frac{nD \Delta t}{(\delta x)^2} (T_a - T_0) = -\alpha (T_a - T_0). \quad (7)$$

The quantity α is called the scaling factor:

$$\alpha = \frac{nD \Delta t}{(\delta x)^2}. \quad (8)$$

The new temperature T'_a of the atoms in the transition layer is given by

$$T'_a - T_a = \delta T = -\alpha (T_a - T_0). \quad (9)$$

From this result we obtain

$$T'_a = (1 - \alpha)T_a + \alpha T_0. \quad (10)$$

Then we scale the velocities of all atoms in the transitional layer so that

$$v_a'^2/v_a^2 = T'_a/T_a. \quad (11)$$

For δx we take the nearest-neighbor distance as a reasonable estimate. The time interval δt must be chosen small enough so that the scaling factor α remains less than one in order to ensure the validity of this scaling scheme. Since scaling of velocities of atoms in the transition layer takes very little computer time, we therefore decide to scale every time step (i.e., $n = 1$) in all cases.

For situations we consider, some extra energy is added to atoms in the computational cell, and we therefore expect heat to flow *out* of the cell into the bulk. Because of temperature fluctuations for the small number of atoms in the transitional layer, however, occasionally T_a is less than T_0 ; in this circumstance our algorithm causes energy to flow back *into*

the cell. This feature is in accordance with the physical behavior of a local region in thermal contact with a heat reservoir provided by the bulk solid. In effect, the atoms in the computational cell now form a canonical, rather than a microcanonical ensemble. Consequently, the proper asymptotic behavior at long times is guaranteed, namely, the temperature of the atoms in the cell and the boundary layer approaches the background temperature T_0 .

Equation (7) has a form similar to Newton's law of cooling: The heat flux is proportional to a finite temperature difference at the boundary of the computational cell. We recognized this similarity, in fact, as we tried to formulate the problem of establishing proper thermal contact between the central cell and the bulk of material. But the situation is a little different for our case, because we want to have a continuous connection between the cell and the surrounding material, rather than an external surface that is usually used for Newton's law of cooling. Our method for introducing the thermal conductivity of the material on a microscopic scale is indicated above. In a MD study of thermal ignition in a reactive hard sphere fluid, a thermal wall is also introduced, partially through consideration of Newton's law of cooling.⁶ But the thermal wall is treated as an external surface, and the rate of heat flow is controlled by conditions imposed arbitrarily at the surface, rather than by the thermal conductivity of the material.

III. MOLECULAR DYNAMICS CALCULATIONS

The atomic interaction used is the well-known Lennard-Jones (6-12) potential. The strength and size parameters are usually taken to be those for argon ($\epsilon = 167 \times 10^{-16}$ erg, $\sigma = 3.4 \text{ \AA}$).⁷ In addition, a hexagonal lattice is used for the 2D system. In most cases, the computational cell contains 100 atoms plus 44 atoms in the transitional layer, with all 144 atoms surrounded by a boundary of four layers of fixed atoms. The positions and velocities of moving atoms are updated at each time step by means of the leap-frog algorithm.⁸ The time step is $\Delta t = 0.05$ ps, compared to the Debye period 0.6 ps.

For the static lattice we calculate atomic spacing, cohesive energy, and compressibility. Then the system is allowed to reach thermal equilibrium at the background temperature T_0 for 300 time steps. The temperature is obtained directly from the average kinetic energy; the vibrational potential energy is calculated by subtracting the cohesive energy of the static lattice. Approach to thermal equilibrium is monitored by observing the expected equipartition of kinetic and potential energy for a classical system. To establish a realistic model, the lattice parameter R_0 is adjusted at each temperature to reduce the external pressure to approximately zero.^{4,9}

After thermalization, extra energy is introduced into the system by increasing the thermal velocity of one atom in the center of the system by a factor of 10. This atom collides with other neighboring atoms; the extra energy gradually diffuses outwards and is partitioned among both kinetic and potential energy. Eventually some extra energy reaches the transitional layer. Velocities of atoms in the transition layer are scaled at each time step to allow energy flow from the cell

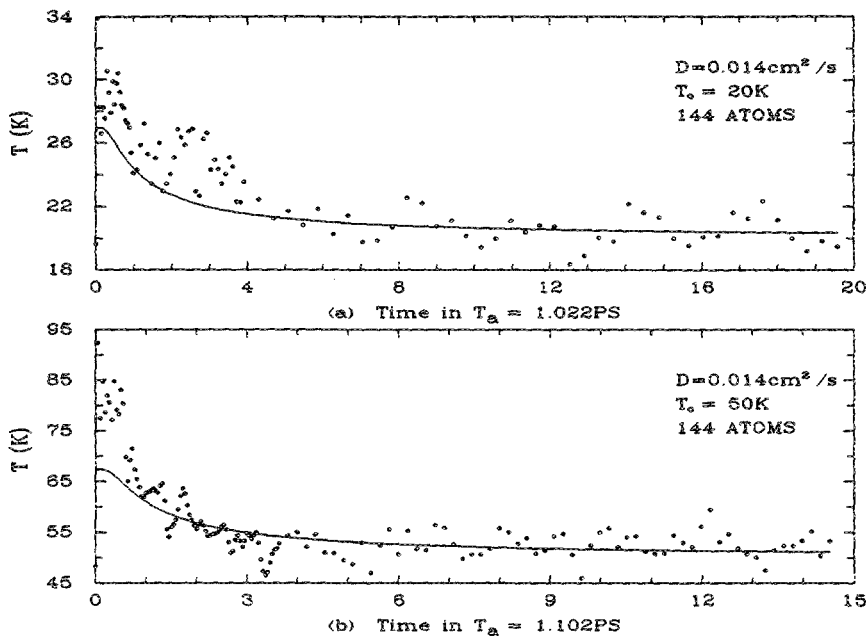


FIG. 1. Molecular dynamics simulation of thermal conduction in 2D LJ solids. The solid curve is the continuum solution. The dots represent the temperature from simulation. (a) The background temperature is 20 K and $R_0 = 3.84 \text{ \AA}$. (b) The background temperature is 50 K and $R_0 = 3.98 \text{ \AA}$. In both cases, the parameters for solid argon are used, and 144 moving atoms are included.

through the transition layer to the bulk. The results of all computer runs, as illustrated in Figs. 1-3, show that the average temperature of the cell is indeed reduced to the original background temperature after a sufficiently long time.

IV. CONTINUUM SOLUTION

We wish to compare these results with the solution obtained from thermal conduction for a 2D continuous medium. First, in simulation of thermal conduction, the area of the computational cell is rectangular. However, in obtaining the solution to the thermal diffusion equation, we assume cylindrical symmetry for simplicity. Therefore, we determine a radius R_a by equating πR_a^2 to the area A of the cell that contains 144 atoms. Second, the central atom is given 10 times the rms thermal velocity in the computer simulation;

this initial condition at $t = 0$ is characterized for the continuous medium by a delta function $T_p A \delta(r)$, in which T_p is the average temperature of each atom measured from the background temperature. Because of equipartition of energy, half of the extra kinetic energy will be converted into potential energy. Thus, the extra energy can be expressed as an average temperature $T_p = 50T_0/N$, where N is the total number of atoms in the computational cell.

The continuum solution for the initial condition discussed above is

$$T(r,t) = \frac{T_p A}{4\pi D t} \exp\left(-\frac{r^2}{4Dt}\right). \quad (12)$$

The average temperature of atoms within a circle of radius R_a is obtained by integration:

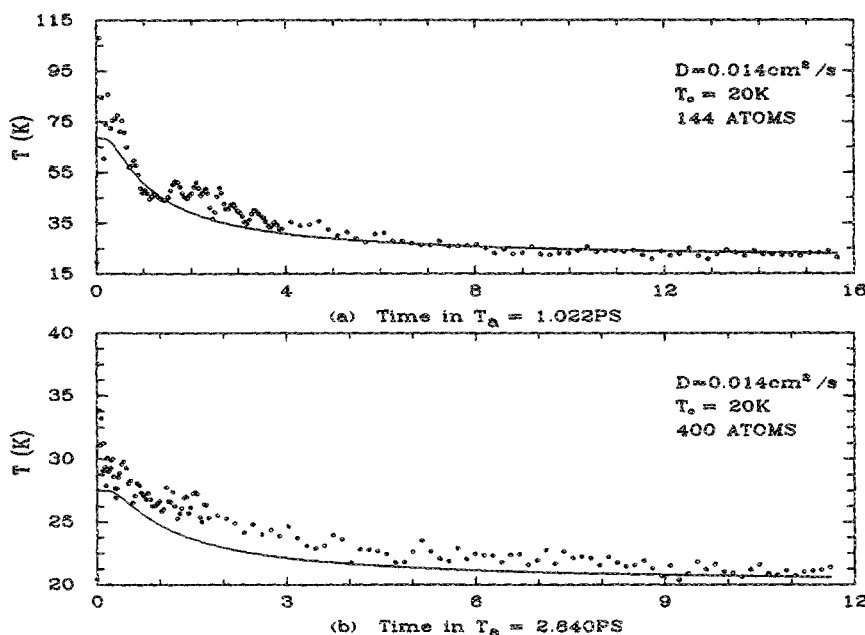


FIG. 2. Tests on different pulse magnitude and size of the computational cell. (a) Velocities of seven atoms in the center of the cell are magnified by a factor of 10, and the other conditions are the same as in Fig. 1. (b) The velocities of three atoms are increased, and 400 atoms are included.

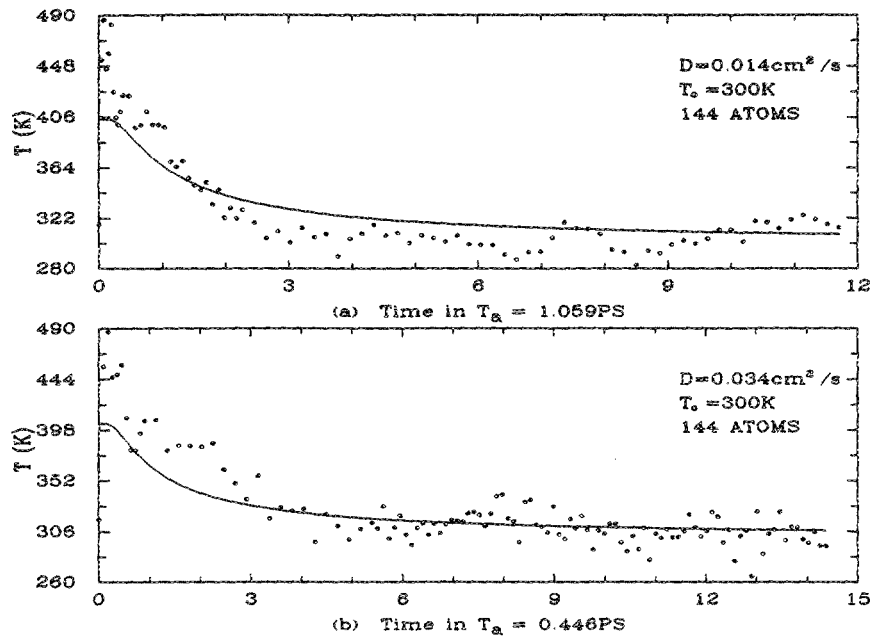


FIG. 3. Effects of different thermal diffusivities on the thermal conduction model for $T_0 = 300$ K. In both cases, the strength parameter ϵ is scaled up to 8ϵ , $R_0 = 3.91 \text{ \AA}$, and the carbon atomic mass is used.

$$T_{\text{avg}} = \langle T(t) \rangle = \frac{1}{A} \int_{R_0}^0 T(r,t) da + T_0$$

$$= T_p \left[1 - \exp\left(-\frac{R_0^2}{4Dt}\right) \right] + T_0, \quad (13)$$

where T_0 is the background temperature. Note that the time scale can be conveniently expressed in terms of $t_a = R_0^2/4D$.

Thus, we obtain a single universal curve for the continuum solution. The length scale R_0 is determined by the size of the local region, and there is a corresponding time scale t_a as defined above. We find, for instance, that $T_{\text{avg}} = 0.65T_p + T_0$ at $t = t_a$, and $T_{\text{avg}} = 0.095 + T_0$ at $t = 10t_a$. In the next section, we investigate the behavior of the MD calculations for changes in various parameters, such as atomic mass and thermal conductivity.

V. DISCUSSION OF RESULTS

The thermal diffusivity is calculated from experimental values of thermal conductivity, specific heat, and density for the system.¹⁰ In most cases, the thermal diffusivity ($D = 0.0143 \text{ cm}^2/\text{s}$) of argon is used, except for Fig. 3(b). Figure 1 displays the average temperature against time in comparison with the continuum solution for background temperatures 20 and 50 K. Since the velocity of the central atom is increased by a factor of 10 at $t = 0$, we use smaller time steps $\Delta t = 0.005 \text{ ps}$ at the beginning of the run to ensure the stability of calculations. After this large velocity decays away through collisions with neighboring atoms, we use relatively larger time steps such as $\Delta t = 0.01$ or 0.05 ps . The temperature T_{avg} is averaged for 144 moving atoms in the system, and it is also based upon a running time average for five or ten time steps. Because of the small number of atoms, there are still noticeable fluctuations in the MD results.

The simulation results indeed show the correct asymptotic behavior for both background temperatures, but there is a discrepancy between simulation results and the contin-

uum solution at short times. The average temperatures of all computer runs are greater than those given in Eq. (13). The disagreement stems from the fact that in molecular dynamics it takes about four vibration periods to convert half of the extra energy to potential energy. After the extra energy is shared by both kinetic and potential energy, both methods yield comparable behaviors.

In Fig. 2(a) we show tests of the size of initial pulse and of the size of the computational cell. For Fig. 2(a) we increase the thermal velocities of seven atoms in the center of the system by a factor of 10. In this case, the initial temperature becomes

$$T_p = 50N_i T_0/N,$$

where N_i is the number of the atoms whose velocities are increased. The result also shows good agreement with the continuum solution. For Fig. 2(b) we include 400 moving atoms, from which 76 atoms are included in the transition layer and 324 atoms are included in the computational cell. In addition, the velocities of three atoms in the center are magnified instead of seven as in Fig. 2(a). No significant change in asymptotic behavior is observed in Fig. 2(b). However, the results from molecular dynamics are a little larger than that of the analytic solution from $t = t_a$ to $t = 4t_a$. This may be attributed to the fact that relatively fewer atoms are included in the transition layer; thus, the scaling is not as effective as in the other cases.

Finally, we study the effects of different values of atomic mass, strength parameter, and thermal diffusivity on the simulation results. The change in the atomic mass has been shown to have no effect on the melting process for alkali halide crystals.¹¹ The strength parameter in the Lennard-Jones potential can be increased to simulate stronger insulators, based upon a corresponding state argument in which the melting temperature is proportional to the cohesive energy. In Figs. 3(a) and 3(b), the strength parameter ϵ is scaled

up to 8ϵ , and the carbon atomic mass is used. In Fig. 3(b), a larger value of thermal diffusivity ($D = 0.034 \text{ cm}^2/\text{s}$) appropriate for a NaCl crystal is used. The simulation results demonstrate reasonable agreement with the continuum solution in both cases at sufficiently long times.

VI. CONCLUSION

We have developed a technique for including a thermal conducting boundary in MD calculations for solids. Tests on various physical parameters and different simulation conditions show no significant effect on the overall behavior. The proper asymptotic dependence at long times establishes agreement between the microscopic and macroscopic treatments of thermal conduction. This study provides a method for accurate inclusion of thermal conduction in simulations of surface melting and in radiation-induced electrostatic disruption of insulator surfaces.

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