

Equilibration of heat conduction simulation in a very thin film using molecular dynamics

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Abstract *This investigation deals with the equilibration of heat conduction simulation in a very thin film using molecular dynamics. Two parameters, the positional order parameter and the kinetic H-function, are employed simultaneously to monitor the evolution to the equilibrium. With the different boundary conditions, material parameters, and molecular lattice configurations, the results of the simulation show that the combination of the two parameters can give a consistent prediction to the approach of the equilibrium. At the equilibrium state, the process of heat conduction in a thin film is studied to understand the macroscopic behaviour from the standpoint of molecular dynamic motions. The method used can be applied to solve other microscopic flow and heat transfer problems using molecular dynamic simulation.*

Nomenclature

F = force acting on lattice
 H = H-function
 k = Boltzmann's constant
 m = mass
 N = number of lattice particles
 q = heat flux
 r = distance between particles
 T = temperature
 t = time
 v = velocity

x = co-ordinate
 λ = position order parameter
 Φ = potential energy
 ε = potential parameter
 σ = potential parameter

Subscripts

Ar = Argon
 i, j = position of atoms
 x = x -component
 O = initial

1. Introduction

Advancement of technologies in microelectronics and downsizing of mechanical components in micro-machines are pushing toward their physical limitations. Today, research on micro-electromechanical system (MEMS) is exploring diverse applications which intimately involve the dynamics of fluid flow and heat transfer in microscale geometries. Better understanding of microscale flows and heat transfer will help to assess the combined influences of mechanical, electromagnetic, thermal, optical and fluid properties and processes.

Molecular dynamic methods are now orthodox means for simulating molecular scale models of matter. The essence of molecular dynamics simulation methods is simply stated: numerically solve the N-body problem of classical mechanics. The methods were originally devised in the 1950s, but they only began to receive widespread attention in the mid-1970s, when digital computers became powerful and affordable. Although a substantial amount of

effort has been expended to determine the molecular forces or potentials in the field of physics and chemistry (Goldstein, 1980; Gray and Gubbins, 1984; Haile, 1992), there has been little work to date on the study of the phenomena in the field of engineering fluid dynamics and heat transfer. Only in recent years, a few works briefed the theoretical background and showed the results of molecular simulation of the problems (Beskok *et al.*, 1996; Kotake and Kuroki, 1993; Kotake and Wakuri, 1994). However, it is an indubitable fact that mechanical phenomena must be understood fundamentally from the elementary process of molecular motions due to the advance of manufacturing and application technology (Kotake, 1995).

In simulation of heat and fluid flow using molecular dynamics, certain operational difficulties are encountered in equating molecular dynamics results to the desired time average such as temperature and velocity. As problems arise in mechanical phenomena such as manufacturing, fluid motion and heat transfer, the prominent difficulties include:

- (1) How long must the sample time be?
- (2) How do we ensure that the phase point samples regions of phase space are “representative” of the equilibrium state?
- (3) How do we identify equilibrium in molecular dynamic simulation?

The application of molecular dynamic theory to an engineering problem may not be able to directly answer these questions, since many solutions of mechanical engineering problems are beyond the comprehension with isolated knowledge of pure sciences. The problems have to be solved from the integrated standpoints of such knowledge as mechanical engineering.

The present study attempts to approach the problems by considering a case of heat conduction in a very thin film (approximately ten to 25 layers of lattice particle) using molecular dynamics method. The particle motion in the solid film is solved numerically to study the transfer process of thermal energy. The objective is to study the behaviors of equilibrium with the effects of various boundary conditions, material parameters, and molecular configuration in a very thin film. The results from the simulation are then analysed to achieve some fundamental understanding of characteristics of molecular dynamic simulation in the microscopic heat transfer problems.

2. Mathematical model

In the microscopic problems of heat removal, especially the heat conduction in a very thin film of solid atoms, the thermal energy is transferred mainly as potential energy. The potential interactions between atoms and molecules play an important role in the heat conduction. In a thin film, if the space domain is large enough that molecular kinetic and potential interaction is confined locally around the molecules without any direct interference from boundary conditions, the linear relationship between heat flux and temperature gradient, which are actually averaged values of molecular motion both in space and time, are

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expected to be continually valid. However, when the space region of atom interaction expands to the whole layer, appreciable effects from boundary conditions of the film might affect the process of energy transfer.

Present numerical simulations are carried out by using Argon molecules because in many respects this inert gas forms the simplest crystals known to us. The Argon crystals are transparent insulators and are weakly bound, with low melting temperature at 84K at atmospheric pressure. The crystal is composed of atoms which have very high ionisation energy and the outermost electronic shells of the atoms are completely filled, and the distribution of electronic charge in the free atom is spherical symmetric.

The method of the molecular dynamic simulation introduced by Kotake (1990) is used to build up the basic mathematical model. A two-dimensional Cartesian coordinate is adopted based on the assumption that the width of the thin film in the z -direction is large compared with the thickness of the film. The lattice is assumed to be free centred cubic (fcc), which is the most common form of crystallised lattice structure for most noble gases. The molecules within the thin film are assumed to have uniform lattice structure as shown in Figure 1.

The lattice particles in a solid film are considered as a point mass and take their motion under van der Waals potential. As the potential between two particles, the Lennard-Jones (12-6) potential is selected due to its simplicity in the expression as well as in the physical meaning of the parameters included. The expression of Lennard-Jones (12-6) potential for Argon is given by

$$\Phi_{ij} = 4\epsilon_{Ar} \left[\left(\frac{\sigma_{Ar}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{Ar}}{r_{ij}} \right)^6 \right] \quad (1)$$

where $r_{ij} = |x_j - x_i|$ is the distance between atoms i and j , $\epsilon_{Ar} = 167 \times 10^{-23}$ J is the potential well, $\sigma_{Ar} = 3.35 \times 10^{-10}$ m is the particle scale and Φ_{ij} is the Lennard-Jones potential. The potential has a minimum value at the point $r_{\min} = \sqrt[6]{2}\sigma_{Ar}$

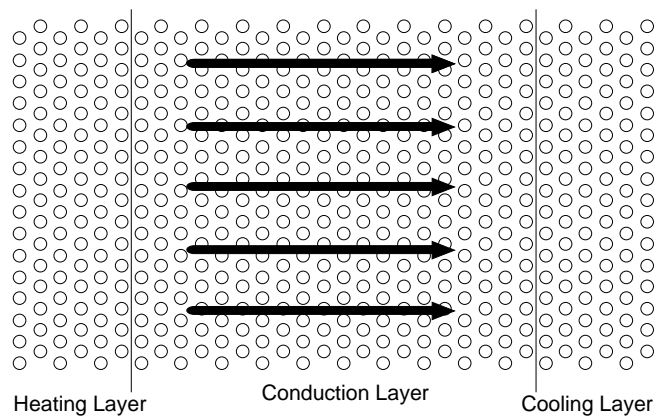


Figure 1.
Model of molecular
particles in a very
thin film

The van der Waals potential is an N-body potential acted on a lattice particle in a solid thin film. To simplify the complicated N-body system, a two-body potential is assumed in the thin film and is expressed as

$$\Phi_i = \sum_j \Phi_{ij} \quad (2)$$

It is assumed that the effect of quantum mechanics is negligible, and particle mechanics is sufficient to describe the motion of the particles. The model is corresponding to matter of low free valance electron, so that the lattice vibration is a predominant mode of conduction as compared to electron diffusion. This assumption is to reduce the complexity of the model involving electron movement in the N-body force field and the quantum effect due to the electrons. Therefore, the force acting on a lattice i is given by

$$F_i = \sum_i (-\nabla \Phi_{ij}) = 24 \frac{\epsilon_{Ar}}{\sigma_{Ar}} \sum_i \frac{x_i - x_j}{r_{ij}} \left[2 \left(\frac{\sigma_{Ar}}{r_{ij}} \right)^{13} - \left(\frac{\sigma_{Ar}}{r_{ij}} \right)^7 \right] \quad (3)$$

Then, the equation of motion of the particle can be written as

$$m \frac{dv_i}{dt} = F_i \quad (4)$$

where $v_i = dx/dt$ represents the velocity of the particle i .

In order to solve the above equations numerically, the finite difference method is used for the time derivative.

The boundary conditions are assigned to two regions at left and right ends in Figure 1, where the particles are heated and cooled respectively. The intermediate is the heat conduction region considered. The layers of particle in this region are changed from ten to 25 layers. Four layers of particles are chosen as the heating and cooling layers. At the layer of four, the force contributed from the particles is of 10^{-4} orders less than those of the nearest particles in layer one. This implies that the boundary conditions imposed by the four layers of heating or cooling particles are sufficient (Kotake and Wakuri, 1994). In the process of heat conduction, the left and right regions of particles in Figure 1 are heated and cooled respectively, by means of constant temperature or constant heat flux.

Periodic boundary conditions are imposed at the top and bottom walls of the film to consider the material of an infinite length, and to remove the constraints in the width of the computational domain.

Initialisation of computing affects the time of equilibration. Prior to the introduction of the heat to the particle systems, an equilibrium state of average temperature is attained by carrying out initial iterative calculation. For a two-dimensional system, temperature is related to the kinetic energy as

$$kT = \frac{1}{2} mv^2 \quad (5)$$

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where k (Boltzmann constant) = 1.38×10^{-23} J/K. The velocity of the particle on average is thus

$$|v_0| = \sqrt{\frac{2kT_0}{m}} \quad (6)$$

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During the initialisation, the particle velocities, which are placed at an equal distance with random directions, are corrected for the system of particles to have the specified temperature in such a way

$$v_i^{new} = v_i^{old} \alpha \quad (7)$$

where

$$\alpha = \sqrt{\frac{T_0}{T}} \quad (8)$$

$$kT = \sum_i^N \frac{1}{2} m v_i^2 / N \quad (9)$$

With this isothermal state, heat is added or removed from the particle system to make the heating and cooling through the thin solid film.

3. Simulation algorithm

To start a simulation, it is efficient to initially locate atoms on a regular lattice structure, preferably the structure into which the substance of interest crystallises. Since Argon crystallises into the fcc structure, the present simulation is started from an fcc lattice. The two-dimensional fcc crystallised lattice is shown in Figure 2.

Samples in the simulation should be taken over a duration equal to several times of the relaxation time for the property. Unfortunately, different properties

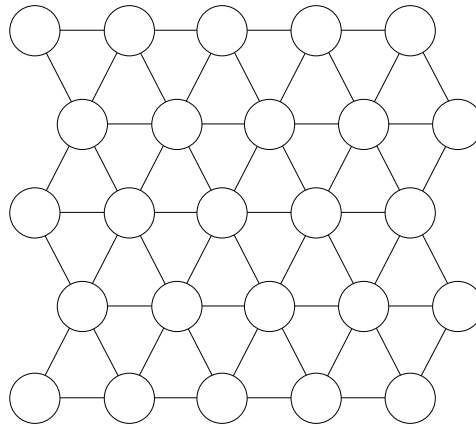


Figure 2.
Two-dimensional
fcc lattice

have different relaxation times. The period of vibrational motion of the Argon particle is about $t = 1 \sim 2$ at the temperature range considered, the iterative time step $\Delta t = 0.005 \sim 0.01$ is then used so that it can resolve the motions in more than 100 steps per period, which is considered sufficient to evaluate the desired time average.

In order to ensure that the phase point sample regions of phase space are “representative” of the equilibrium state, we have to ensure that the phase-space trajectory is not metastable. The method adopted for such metastability checking is to repeat the trajectory calculation using different initial conditions and/or stimulating the system with increases in energy that should drive the phase point over any energy barriers. For example, we tested for metastabilities by introducing an external perturbation, such as temperature excursion. Among the tests, no metastable trajectories were detected.

During the simulation, the equilibrium is monitored by a subroutine invoked during every iteration step. For an isolated system, a necessary and sufficient condition for identifying equilibrium is that the system entropy be a maximum. Unfortunately, entropy is not a measurable property and cannot be readily evaluated from the time average of some mechanical quantities. Hence, other means of equilibrium monitoring have to be found.

The evolution to equilibrium necessarily involves equilibrium in both configuration space and momentum space, so we need quantities that monitor both. Therefore, two numbers are set as conditions for the equilibrium in the present simulation: one that tracks the disorder in atomic positions and a second that tracks the development of the Maxwell distribution of velocities.

To monitor the dissolution of an fcc lattice composed of N atoms, a positional order parameter λ introduced by Verlet (1967) is used. The order parameter in a two-dimensional system is defined by

$$\lambda = \frac{1}{2}(\lambda_x + \lambda_y) \quad (10)$$

where

$$\lambda_x = \frac{1}{N} \sum_i^N \cos\left(\frac{4\pi x_i}{a}\right) \quad (11)$$

and a is the length of one edge of the fcc unit cell. Initially, when all atoms occupy fcc lattice site, $\lambda = 1$ because the positional components x_i, y_i are integer multiples of $1/2 a$; when the lattice is completely dissolved, λ fluctuates about zero because then the atoms are distributed randomly about the original lattice sites. The fluctuations have magnitudes which should not be larger than \sqrt{N}/N . Thus as the fcc lattice dissolves, λ decays from unity to zero.

To monitor the development of Maxwell's velocity distribution, which is a Gaussian with standard deviation $\sigma = \sqrt{kT/m}$ about the mean value of the velocity component at x direction $v_x = 0$, we can compute the velocity distribution $f(v)$ and watch how it evolves through equilibration. It is cumbersome, however, to

monitor the temporal evolution of a function. We would prefer to monitor a single number. Fortunately, a single value is provided by Boltzmann's H-function. Taking one component of H-function to be

$$H_x = \sum_{\Delta v_x} f(v_x) \ln f(v_x) \Delta v_x \quad (12)$$

where $f(v_x)$ is the distribution of the x -component of atomic velocities

$$f(v_x) \Delta v_x = \frac{1}{N} \sum_i^N \delta(v_x - v_{xi}) \Delta v_x \quad (13)$$

The corresponding value of the instantaneous (kinetic) H-function is then

$$H = \frac{1}{2} (H_x + H_y) \quad (14)$$

The two quantities in equations (10) and (14) are employed simultaneously and are programmed in an equilibrium monitoring subroutine. Equilibrium is not complete until λ is fluctuating about zero and the H-function is close to a value that is consistent with the Maxwell velocity distribution.

4. Results and discussion

Simulation has been carried out using different initial and boundary conditions, as well as different molecular layer configurations. Figure 3 shows the results of a 19-layer heat conduction using constant temperature as boundary condition. In Figure 3(a) is the distribution of temperature through the conduction layer at four different times; (b) is the evolution of temperature T_a which is averaged over all the particles in the layer for the same time step. The temperature is non-dimensionalized by taking $T(k/24\epsilon) \rightarrow T$. Under the normal configuration, the heat transfer process is directly compared with macroscopic heat conduction. It is seen from the figure that the temperature is almost linearly distributed through the heat conduction layer as the Fourier law for the macroscopic heat conduction. The gradient of the temperature distribution determines the thermal conductivity.

The equilibration is monitored by the instantaneous values of the translational order parameter λ and Boltzmann's H-function as shown in Figure 3(c) and (d). The time required for λ to exhibit stable fluctuation about zero depends on the packing fraction and on how the initial velocities are assigned. In Figure 3(c), it is found that λ is fluctuated within the magnitude of ± 0.0574 after some 11,000 time steps. The equilibrium is also confirmed by H-function development in Figure 3(d), which is an instantaneous H-function computed from equation (14). The dash-dot line in Figure 3(d) is a curve-fit using a least-squares algorithm. The result shows that the H-function decays in monotone fashion and asymptotically approaches the Maxwell value.

Simulation results using the constant heat flux boundary condition $q = 2.02 \times 10^{-4} \text{ W/m}^2$ is shown in Figure 4. The constant energy is given to the heating

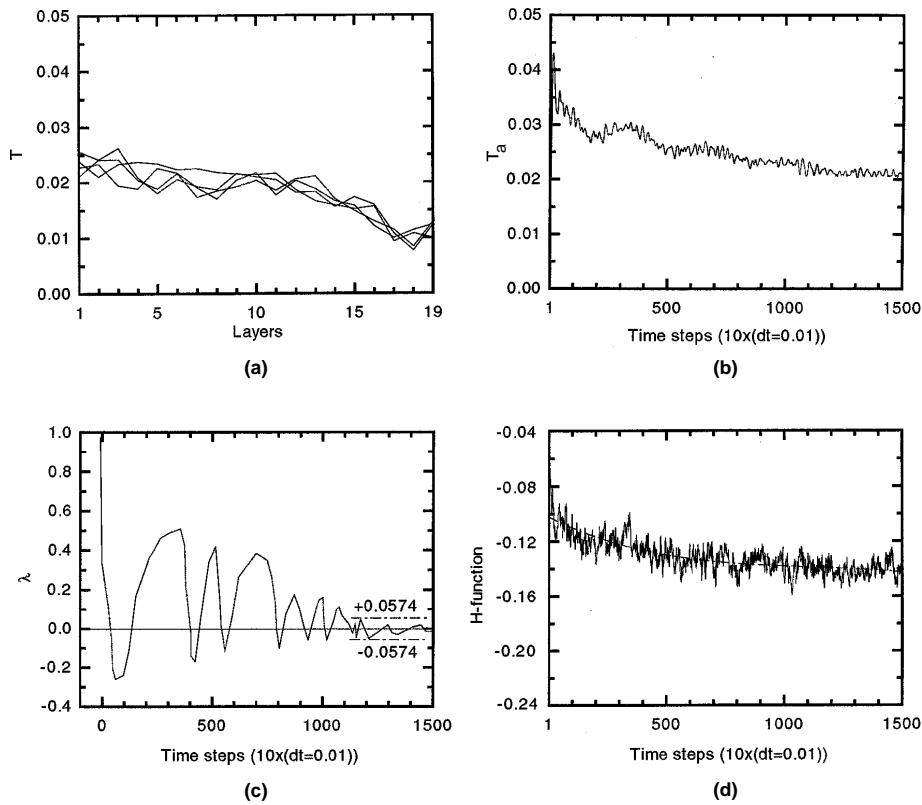
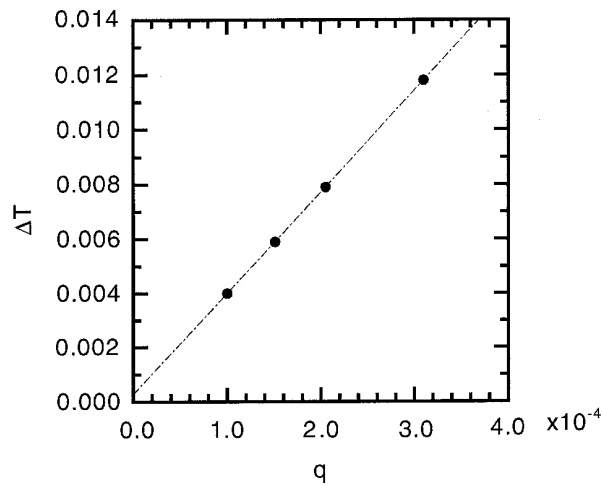


Figure 3.
Simulated results for
72.6K/29.0K
temperature difference
over 19 lattice particle
layer: (a) temperature
distribution;
(b) average temperature;
(c) positional order
parameter;
(d) H-function

layers and the energy of the same amount is subtracted from the cooling layers. To control the heat flow, an algorithm is built up to ensure that the heat removed from the cooling layers does not exceed the total amount of heat energy available at the cooling region. As shown in Figure 6(a), the temperature distribution is linear within the conduction layer. The equilibrium is achieved after about 12,000 time steps.

The equilibration behaviour for both constant temperature and heat flux boundary conditions is similar. The evolution of the order parameter λ in Figure 3(c) and Figure 6(c) show that the initial fcc lattice was quickly destroyed, but remnants persisted over about 10,000 time steps, after that, the remnants were dissolved and λ , was fluctuating about zero. For both boundary conditions, the equilibration predicted by λ and H-function agree with each other. The instantaneous H-functions in Figure 3(d) and Figure 6(d) began to decay toward its equilibrium value after about the same time steps as the λ which started to fluctuate within the magnitude \sqrt{N}/N . The approach of the H-function is in a gradual monotone fashion, there is no evidence that metastabilities exist in the momentum space. In Figures 3(b) and 6(b), the averaged temperature T_a also approaches to a

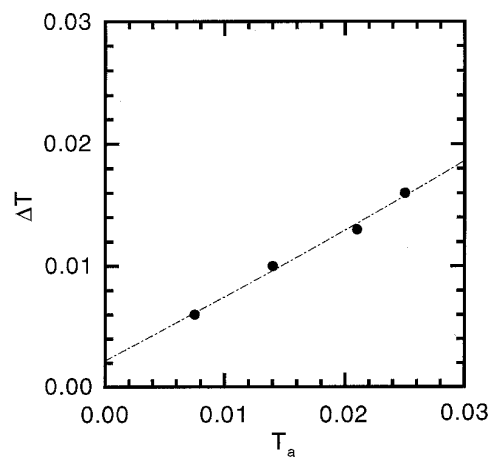
Figure 4.
Relationship between
heat flux and
temperature difference



stable value after about 12,000 time steps. This coincidence confirms the approach and existence of the equilibrium state in the simulated cases.

The linear relationship of the temperature gradient versus different heat flux input is seen in Figure 5. This agrees with the Fourier's law in the macroscopic heat transfer. Since the molecular particle scale for Argon is $\sigma_{Ar} = 3.35 \times 10^{-10}$ m and ten to 25 layers of particles are considered, the macroscopic heat conduction behaviour is expected to be valid in a thin film in nano-meter order thickness. The linear distribution of the temperature difference also implies that thermal conductivity is independent of the heat flux. However, as shown in Figure 6, at a given heat flux, increasing the average temperature in the layer results in higher temperature difference or lower thermal conductivity. This indicates that in the molecular level, thermal conductivity is still a function of the averaged material temperature as that in the macroscopic phenomena. These results also agree with the study by Kotake and Wakuri (1994).

Figure 5.
Relationship between
averaged layer
temperature and
temperature difference



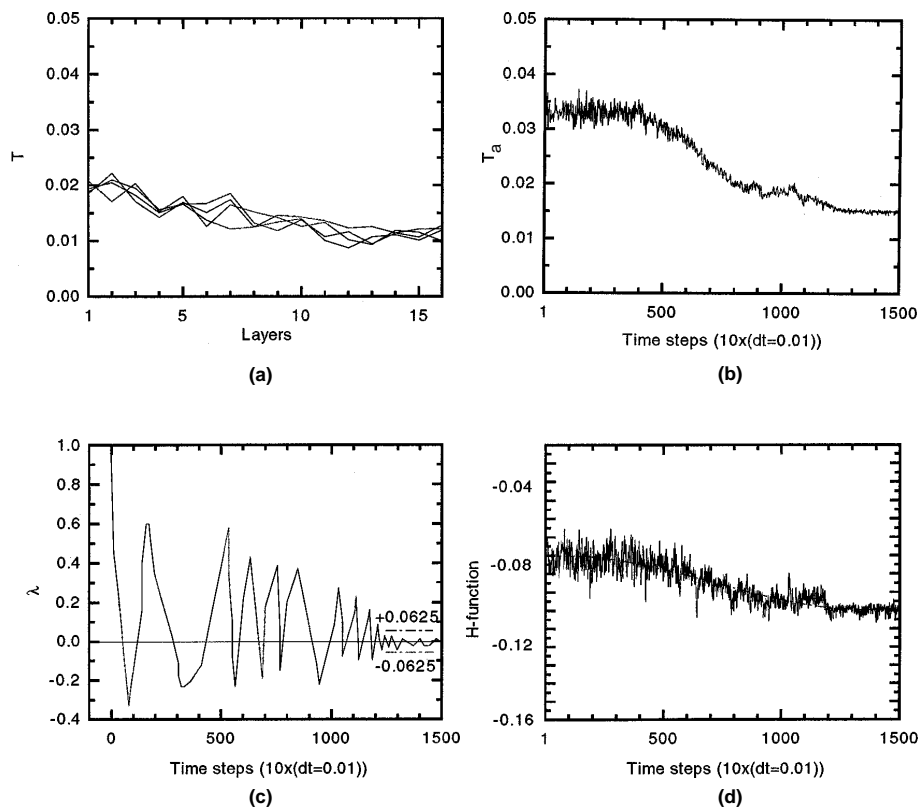


Figure 6.
Simulated results for
heat flux 2.1×10^{-4} over
16 lattice particle layer:
(a) temperature
distribution; (b) average
temperature;
(c) positional order
parameter;
(d) H-function

The equilibration behavior in different simulation configurations such as heat conduction across two materials and placing void particles in the thin film were also studied in detail. Figure 7 shows the heat conduction across the thin film which consists of two layers of material with different molecular mass. The second half of the layers (layers 7 ~ 14) has molecular mass twice that of the first half (layers 1 ~ 6). As a result, the temperature gradient for the first half of the thin film is approximately double the temperature gradient for the second half of the thin film due to the different thermal conductivity of the two materials.

Figure 8 shows the simulated results from existence of bubbles or defects in the seventh layer of the thin film. The algorithm of the simulation is similar to the original model except five particles were removed from the thin film by simply excluding them during the iteration steps. It is found in Figure 8(a) that a sudden drop happened to the temperature gradient, while the gradient after that remained the same.

The equilibration in the above two configurations is similar to the normal configuration, except in Figure 7, the equilibrium was quickly achieved after only about 6,000 time steps. This means that the basic behaviour of the equilibration for the heat conduction in a thin film is not affected by the change of the molecular configuration in the way of different material or material defects.

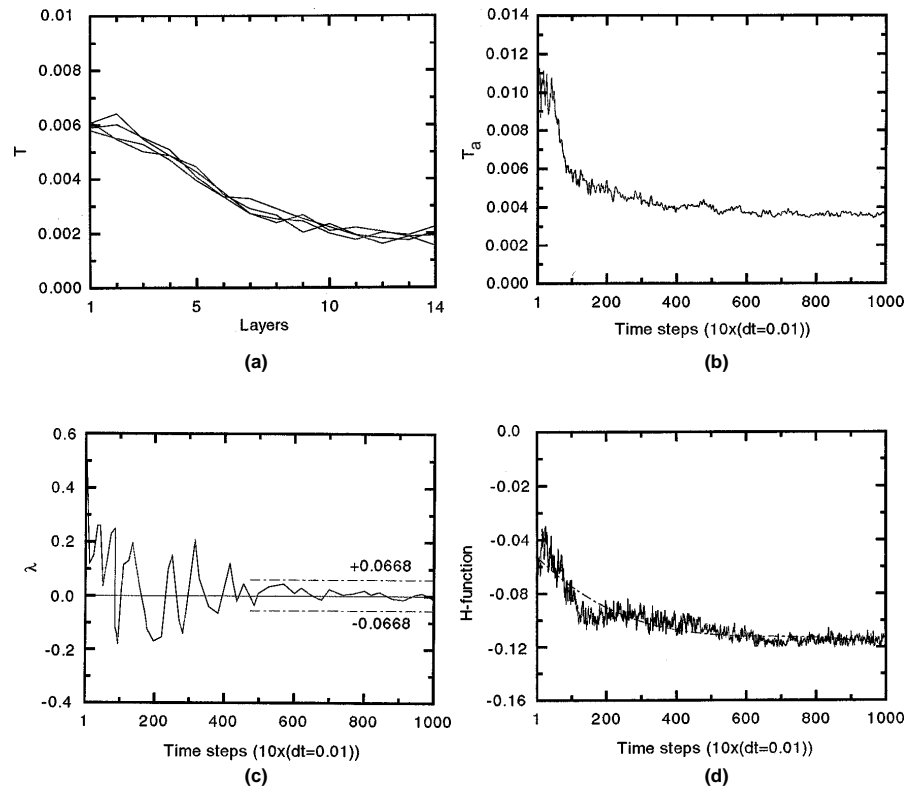


Figure 7. Simulated results of heat conduction across two materials for 17.43K/5.81K temperature difference over 14 lattice particle layer: (a) temperature distribution; (b) average temperature; (c) positional order parameter; (d) H-function

5. Conclusion

To study the heat conduction in a very thin film, the evolution to equilibrium is successfully monitored by two parameters. The positional order parameter λ is used to monitor the disintegration of the initial fcc lattice, and it should be fluctuating about zero with fluctuation having magnitudes $\leq \sqrt{N}/N$. The instantaneous Boltzmann H-function is used to monitor the development of the equilibrium distribution of atomic velocities, and it should approach a value consistent with the Maxwell distribution. The combination of using these two parameters confirms the approach and existence of the equilibrium state under the conditions used in the present simulation. The time required for equilibration may vary from different molecular configurations and boundary conditions, but the basic behaviour of equilibration is independent of these factors. The thermodynamic property such as temperature is independent of how the equilibrium state is attained. The obtained results provide useful information for solving molecular scale flow and heat transfer problems by molecular dynamic simulation.

At the equilibrium state, the heat conduction in a very thin film is studied. Within the thickness range of the molecular layers, the results obtained are in agreement with macroscopic heat conduction, compared to the Fourier's law. The numerical simulation shows that for heat conduction of thin films, the temperature gradient increases linearly with respect to the heat flux and the

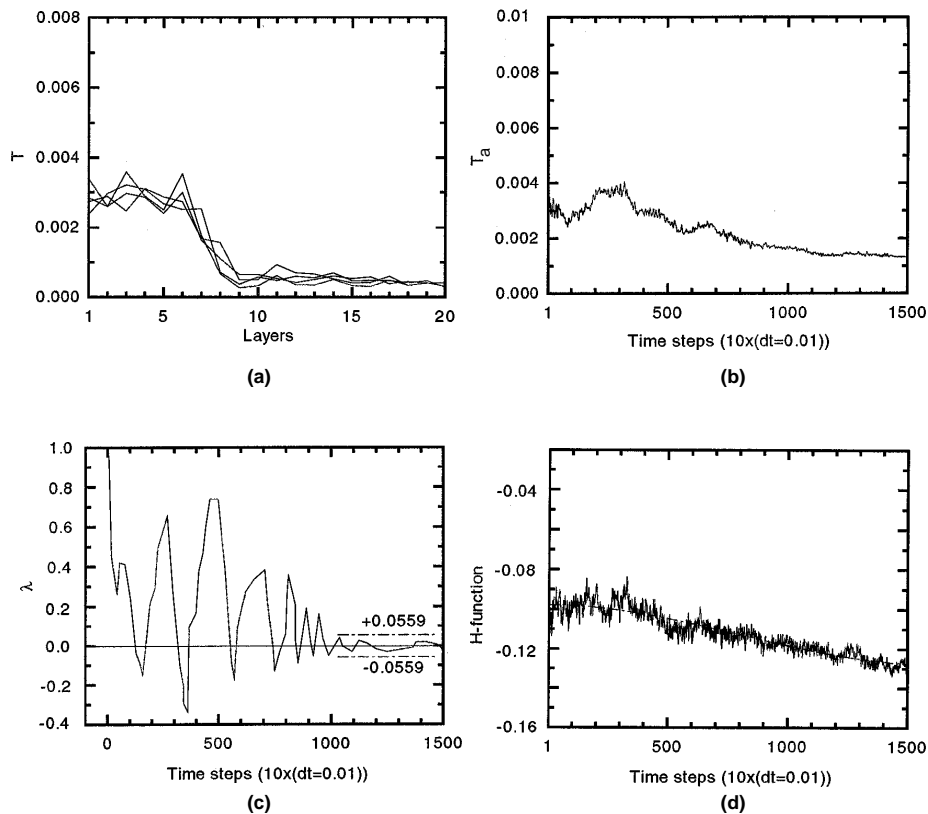


Figure 8.
Simulated results of
heat conduction in a
thin film with five
particles removed from
the seventh layer for
8.71K/1.16K:
(a) temperature
distribution; (b) average
temperature;
(c) positional order
parameter;
(d) H-function

averaged temperature of the material. These relationships are independent of film thickness and the initial temperature.

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