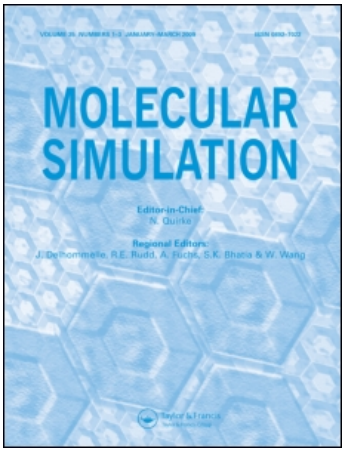

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Molecular dynamics study of the thermal conductivity of nanoscale argon films

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Molecular dynamics study of the thermal conductivity of nanoscale argon films

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Non-equilibrium molecular dynamics (MD) simulations were used to study the thermal conductivity of thin argon films. The MD simulations show that the argon film's thermal conductivity is affected by the thickness up to thickness of about 100 nm, which agrees with theoretical estimates. The results show that the MD method is very effective for modeling nanoscale thermal conduction. Besides pure argon films, the effect of vacancies on the argon film's thermal conductivity was also studied. The vacancies greatly reduce the thermal conductivity as a function of the vacancy concentration but not as a function of the vacancy distribution when the film's temperature is constant.

Keywords: Molecular dynamics; Thermal conduction; Thin films; Vacancies

1. Introduction

Nanoscale dielectric films are now important components of microelectronic and photoelectronic devices. The analysis of the thermal conductivity of dielectric films is very important for the design of microelectronic and photoelectronic devices. In nanocsale films, the size is comparable to the mean free path of the phonons, so the thermal properties are affected by the system size. Therefore, microscale and nanoscale films has been a key focus of international heat transfer research in the past two decades [1–2].

Theoretical analyses of microscale and nanoscale thermal conduction are based on the Boltzmann transport equation (BTE) and kinetic theory. Solutions to the BTE are obtained: using Monte Carlo methods to obtain the solution [3], by directly solving the BTE as a partial differential equation [4], or by using modes from phonon radiation heat transfer. The BTE approach needs some assumptions to simplify the phonon scattering process, so the precise solution of the BTE is based on a good understanding of the phonon scattering progress. According to the kinetic theory of phonon gases, the thermal conductivity of the solid state is given by

$$k = \frac{1}{3} c_v v^2 \tau \tag{1}$$

where c_v is the specific heat per unit volume, v is the average speed of sound and τ is the phonon's mean free path between phonon scattering events. Several studies [5–7] have focused on the analysis of τ.

Molecular dynamics (MD) simulations have also become a hot tool for studying nanoscale thermal conduction. In MD methods, the positions and momentum space trajectories of a system of particles are calculated by solving Newton equation of motion for all the particles. Besides the potential mode, no assumptions are needed to simulate the heat transfer. Several studies have given MD results for the thermal conductivity of dielectric films [8,9]. These simulations report that the thermal conductivity of nanoscale dielectric films shows a size effect with the thermal conductivity lower than the bulk value and decreasing as the film's thickness decreases. However, to our knowledge none of the MD results have given the size at which the film size effect disappears.

Real crystals always contain defects such as impurities, vacancies and dislocations which reduce the thermal conduction due to phonon scattering by the defects. However, in reality, the effect of defects on the thermal conduction cannot be easily studied because the fraction of the thermal resistance caused by the defects cannot be specified. However, in MD simulations, defects can be

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artificially constructed to study the thermal resistance caused by the defects. Several MD studies [10,11] have analyzed the effects of defects on the thermal conductivity, but these studies all focused on the properties of the bulk materials.

Non-equilibrium MD simulations were used in this study to investigate the cross-plane thermal conductivity of argon films at 40 K with thickness ranging from six to more than one hundred nanometers with emphasis on the size effects. This paper also studies the effects of defects on the thermal conductivity of argon thin films using the MD method.

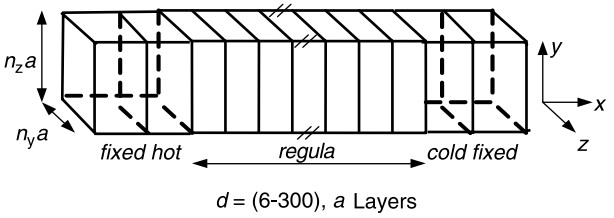

Figure 1. Schematic diagram of model system for heat conduction of thin argon films.

2. Physical–mathematical model and simulation method

The classic MD method only simulates the lattice vibrations which dominate the thermal conduction in an insulator, which assumes that the contribution from electrons is negligible. As we know the energy of a lattice vibration is quantized. The quantum of energy is called a phonon. To study phonon heat conduction, the present paper chooses argon solid thin film as study object. Another important reason why choose argon is the availability of a good intermolecular potential for argon. The widely accepted Lennard–Jones 12-6 (LJ) potential matches experimental data for bulk argon reasonably well. Additionally, results using the LJ potential to study solid thin films can be compared with other existing works on argon-type systems.

In the MD methods, the thermal conductivity is computed using either equilibrium MD [10–14] which uses the Green–Kubo method or non-equilibrium MD [8,15,16] which uses the so-called "direct method". The non-equilibrium MD method imposes a temperature gradient across the simulation cell which is analogous to the experimental conditions, so the non-equilibrium MD method was used in the present work.

In the non-equilibrium MD method, two methods can be used to simulate the heat conduction process. One is to apply a constant heat flux to the solid system, then calculate the resulting temperature gradient and finally determine the thermal conductivity by a simple ratio of the flux to the temperature gradient. The reverse method is to keep the system boundaries at constant temperatures and calculate the resultant heat flux. The latter method is used in the present study because the mean system temperature is easier to control than in the first method. The simulation model is illustrated in figure 1. In this model, periodic boundary conditions are used in the z and y directions. Along the cross-plane direction, the x direction, each atom is assigned a type according to its spatial position: "fixed", "hot", "regular", or "cold". The fixed atoms are stationary during the whole simulation and they serve as adiabatic boundary conditions. The "hot" and "cold" atoms are the temperature control boundary conditions where the velocities of each atom are controlled to maintain the desired temperature. In the regular part, besides LJ potential mode, no special control is performed to the atoms.

At the beginning of each run, all the non-fixed atoms are given initial temperatures by choosing their velocities based on the Maxwell distribution at the given temperature. Then the motion equations for each atom are resolved using the widely used "velocity Verlet" algorithm. The new position of each atom is calculated from its old position, velocity and force. The force is the derivative of the potential energy of each atom. The LJ potential is written as

$$\phi(r_{i,j}) = 4\varepsilon\left[\left(\frac{\delta}{r_{i,j}}\right)^{12} - \left(\frac{\delta}{r_{i,j}}\right)^{6}\right] \tag{2}$$

where ε is the well depth parameter, δ is the equilibrium separation parameter, and $r_{i,j}$ is the distance between two atoms. Only the neighbors of an atom within a certain cutoff radius, $2.6\delta_{\mathrm{LJ}}$, are included in the force calculations because far away atoms have negligible effect on the total force.

As well known, during MD simulations, the force calculation is the most time consuming part. The neighbor cell list method was used in this study as an efficient way to reduce the computational time. The film temperature distribution was obtained by dividing the entire film into layers along the x direction. The number of the layers depends on the film thickness. In this paper, the temperature of each layer was calculated using the formula,

$$T = \frac{\sum_{i=1}^{N} m_i v_i^2}{3Nk_{\mathrm{B}}} \tag{3}$$

where N is the number of atoms in the layer. That is the temperature in each layer is calculated from the squares of the atomic velocities in that plane summed in accordance with the equipartition principle. The heat flux was calculated from the change in the kinetic energy of the hot and cold atoms during each simulation time step,

$$\Delta E = \pm\frac{1}{2}m\sum\left(v_{\mathrm{old}}^2 - v_{\mathrm{new}}^2\right). \tag{4}$$

The minus sign is for the higher temperature boundary while the plus sign is for the lower temperature boundary.

Table 1. Simulation parameters.

Parameter	*Value*
LJ well depth	1.67×10^{-21} J
LJ equilibrium separation	3.4×10^{-10} m
Boltzmann's constant	11.38×10^{-23} J/K
Argon atomic mass	66.3×10^{-27} kg
Lattice constant	5.304×10^{-10} m
Time step	10 fs
Cross-sectional unit cells	6
Unit cells in each hot or cold region	2
Unit cells in each fixed region	3

An important issue in MD simulations is identifying when the simulation is at equilibrium. In the present study, equilibrium was based on the relative difference between the heat fluxes at the hot and cold boundaries. The simulation was assumed to be in equilibrium when the relative difference was less than 20% [17].

Based on the Fourier law, the thermal conductivity of the argon film is:

$$k = \frac{\Delta E_{\text{hot}} + \Delta E_{\text{cold}}}{2\tau A|\nabla T|}$$

where τ is the simulation step time, A is the cross sectional area and $|\nabla T|$ is the absolute value of the temperature gradient in the cross-plane direction. The standard LJ dimensionless length, temperature and energy were used in the simulations. The critical input parameters for the simulations are listed in table 1. The time step used is 10 fs, which is somewhat large. Simulations were conducted with time steps to confirm the time step of 10 fs was sufficient small to give accurate results. The results in table 2 shows the time step of 10 fs was small to give accurate results. To get reliable results, the simulations were run at least one million time steps, which is 10 ns.

3. Simulation results for pure argon films

In this study of pure argon films, the mean temperature of the simulated films was 40 K with the higher temperature end at 50 K and the lower end at 30 K. Figure 2 shows the temperature profile across a 20 nm thick film along the cross-plane direction. Three properties can be found from the figure: (1) the temperature of higher temperature end is actually lower than the set one and at the lower temperature end the situation is reverse. This phenomenon is physically reasonable. When the hot and cold boundaries are controlled at desired temperatures, energy is "input" into the hot boundary and "output" out from the cold boundary.

Table 2. The predicted thermal conductivities for various time steps.

Film thicknes (nm)	*Time step (fs)*	*K (W m/K)*
6.348	10	0.559
6.348	5	0.559
6.348	2	0.551

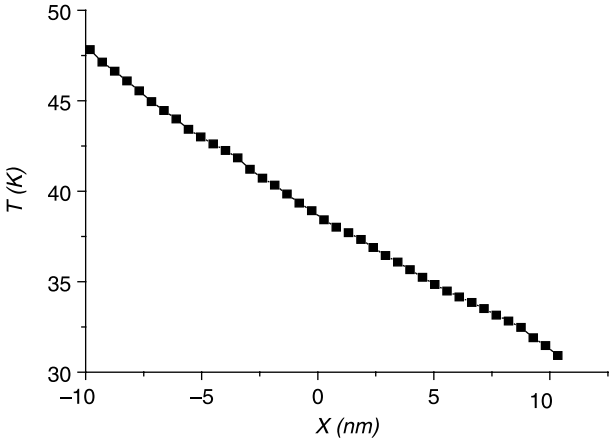

Figure 2. Temperature profile in 20 nm thick film.

The temperature difference is therefore a natural result of the heat transfer; (2) in the middle of the domain away from the two boundaries, the temperature profile is nearly linear, which shows that the Fourier law is still valid. The small non-linear effects occur because the thermal conductivity of argon is a function of the temperature; and (3) the temperature gradients at the hot and cold boundaries are larger than in the rest of the film, which indicates a thermal boundary resistant at these two zones.

A series of simulations were conducted to study the size effect on the film's thermal conductivity. The number of regular atoms was changed to construct various thickness films, with thicknesses ranging from six to more than one hundred nanometers. The relationship between the thermal conductivity and the film thickness in figure 3 shows that the thermal conductivity of the thin films is lower than the bulk thermal conductivity and decreases with decreasing film thickness. At smaller thicknesses, the thermal conductivity increased very rapidly with thickness. For example, from 3 to 20 nm, the thermal conductivity increases by nearly 0.2 W/m K; However, from 40 to 160 nm, the thermal conductivity only increases by 0.1 W/m K. This trend indicates that at different thickness ranges, the film's thickness has different effects on the thermal conduction. Finally and most importantly,

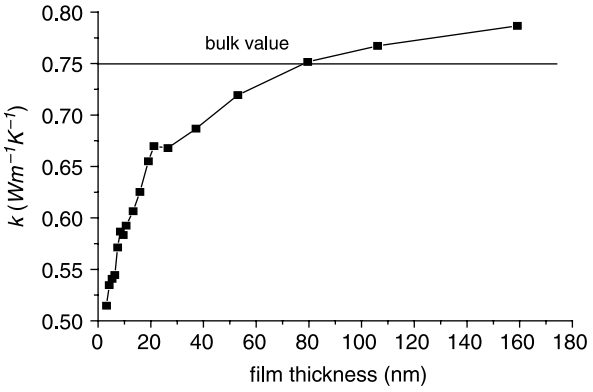

Figure 3. Thermal conductivity of argon films at 40 K.

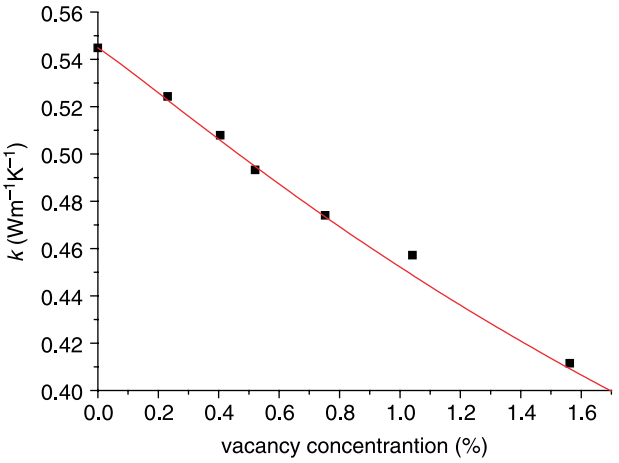

Figure 4. Thermal conductivity of 6.38 nm thick film with various vacancy concentrations, the solid line is a fit to equation (7) where A is 29.464 and α is 1.079.

the simulations show that the size effect becomes negligible for the film whose thickness is more is about 100 nm. According to the following formula [18]

$$\frac{1}{k} = \frac{a^3}{4k_B v}\left(\frac{1}{l_\infty} + \frac{4}{L_Z}\right) \tag{6}$$

where a is the lattice constant, k_B is Boltzmann constant, v is the speed of sound, l_∞ is the phonon mean free path in the bulk material and L_z is the system size, which for thin films is the film thickness. As a rough estimation, when L_z is about $40l_\infty$, the thermal conductivity is about the bulk's value. For argon, the phonon mean free path in the bulk material is 3.4 nm [19], so for the argon film, the size effect will become negligible for the film thickness is about 130 nm which agrees reasonably with the present simulation results. This result further illustrates the reliability the MD method for studying phonon thermal conduction in nanoscale films.

4. Argon films with defects

Real films always contain defects including isotopes, vacancies and dislocations which reduce the phonon heat transfer. The MD simulations were also used to predict the thermal conductivities of argon films with vacancies. Vacancies were modeled as defects to avoid the difficulties of different potential model for another kind of material. The vacancies in the film were formed by randomly removing a selected number of atoms from the perfect FCC lattices. The simulated average temperature was still 40 K.

The effect of the vacancy concentration on the thermal conductivity for a 6.3 nm film at 40 K is shown in figure 4. The vacancy concentration was changed by changing the number of atoms randomly moved from the lattice. The results show that the vacancies greatly reduced the thermal conductivity in a somewhat non-linear way. Assuming that vacancy scattering is independent of the acoustic scattering which is dominant in a pure perfect crystal, the total phonon scattering length can be written as

$$L_{tot}^{-1} \approx L_{pure}^{-1} + L_{vac}^{-1} \tag{7}$$

where L_{pure} denotes the scattering length in a perfect crystal and L_{vac} denotes the scattering length induced by the vacancies. Further assuming that the sound speed and heat capacity are not affected by the vacancies, then

$$k_{tot}(n_v) = \frac{k_{pure}}{1 + k_{pure}/k_{vac}}. \tag{8}$$

The results in figure 4 can then be fitted as

$$k(n_v) = \frac{k_{pure}}{1 + An_v^\alpha} \tag{9}$$

where n_v is the vacancy concentration and A and α are constants. A least square analysis of the simulation results give A as 29.464 and α as 1.079. This suggests that k_{pure}/k_{vac} is approximately $29.464\ n_v^{1.079}$.

The effect of film thickness on the effect of vacancies was also investigated using a series of simulations in which the vacancy fraction was always 1% with the film thicknesses ranging from 3 to 26 nm. The results in figure 5 show that for various thicknesses, the ratio of the film's thermal conductivity to that of a perfect film was nearly constant at 0.8.

The vacancies reduce the thermal conductivity because the vacancies destroy the regularity of the perfect lattice. Based on the kinetic theory, the disrupting of the regularity of the lattice increases the resistance to the motion of the phonons which is the dominant heat transfer mechanism in solid argon.

The effect of the random distribution of vacancies on the thermal conductivity was also investigated by again randomly distributing the vacancies in the film while maintaining the same number of vacancies. The results for two film thicknesses, 6.3648 and 7.4256 nm in figure 6 show that the vacancy distribution in the film had little effect on the thermal conductivity. Therefore, the thermal

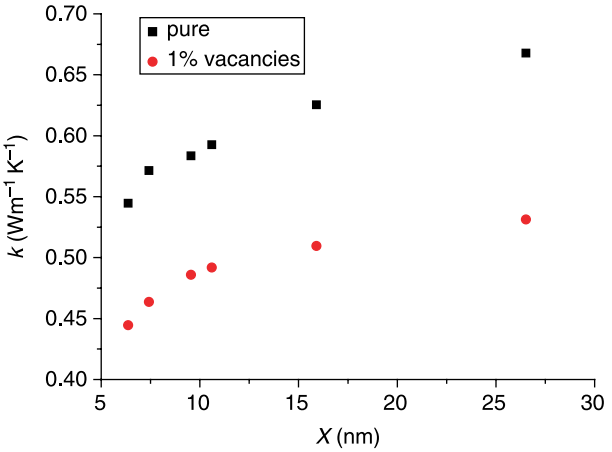

Figure 5. Effect of vacancies on the thermal conductivity of argon at 40 K.

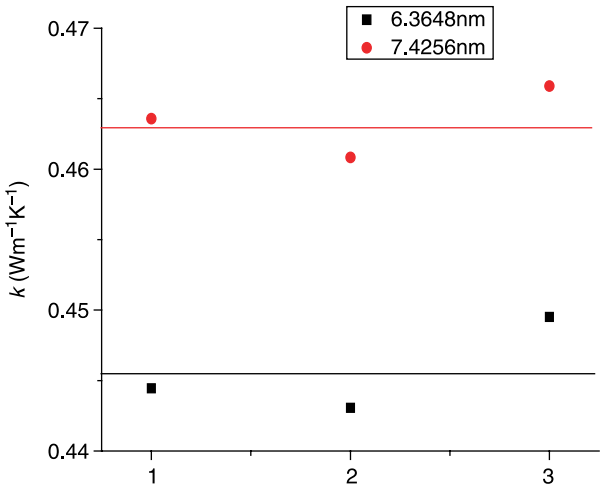

Figure 6. Thermal conductivities for various vacancy distributions, the horizontal ordinate stands for different vacancy distributions.

conductivity only depends on the vacancy concentration when the temperature is constant.

5. Conclusions

The non-equilibrium MD method was used to simulate the thermal conductivity of argon thin films. The results show that the film's thermal conductivity increases with increasing thickness, but that the rate at which the thermal conductivity increases differs for different film thickness ranges. The simulations also show that for argon, the size effect become negligible when the film's thickness is about 100 nm, which agrees with theoretical estimates. Thus, the results verify that MD simulations are a useful tool for modeling thermal conduction in nanoscale films.

The effect of vacancies on the argon film thermal conduction was also studied. The vacancies were found to greatly reduce the film's thermal conductivity due to the vacancies disrupting the regularity of the argon lattice. The number of vacancies affects the thermal conductivity but the vacancy's distribution has little effect on the thermal conductivity. The relationship between the thermal conductivity and the vacancy concentration was found to be

$$k(n_{\mathrm{v}}) = \frac{k_{\mathrm{pure}}}{1 + An_{\mathrm{v}}^{\alpha}}$$

with $A = 29.464$ and $\alpha = 1.079$. In addition, the thermal conductions of films with different thicknesses were reduced by the same percentage for a given vacancy concentration.

Acknowledgements

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