MOLECULAR DYNAMICAL CALCULATIONS OF THE THERMAL DIFFUSIVITY OF A PERFECT LATTICE

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We have used the method of molecular dynamics to make a detailed study of thermal diffusivity in a perfect monatomic lattice. The interatomic potential is that appropriate for iron. We limit the atomic motions to two dimensions in order to shorten the computation. We maintain one end of the lattice at a given kinetic temperature and obtain the temperature profile in the lattice as a function of time. The total energy added to the system is recorded. We fit diffusive curves to the temperature profiles and thus obtain the thermal diffusivity of the lattice. Its value is 4×10^{-6} $m^2 sec^{-1}$ at a mean lattice temperature of 75K.

1. INTRODUCTION

We have used the method of molecular dynamics to study the transport of thermal energy in a perfect monatomic lattice. The complexity and immensity of such calculations make it desirable to relate our results to physical reality in as many ways as possible. To this end, we obtained a rough estimate of the lattice thermal

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conductivity from an earlier calculation of heat pulse propagation in a three-dimensional lattice[1]. This led to the present, more detailed study of thermal diffusivity in a lattice. We have limited the atomic motions to two dimensions in order to shorten the computation time, otherwise, this restriction is insignificant.

We shall first describe our model, then in section 3 we shall treat the problem using conventional theory of heat transfer by diffusion in a continuum. In section 4 we present the results of our molecular dynamical calculations and compare them with the continuum theory. In the final section we discuss our results.

2. MODEL

Our two-dimensional system is made up of bcc unit cells forming a ribbon-like filament 25 units wide, 250 units long, and 1 unit thick. This ribbon is placed in Cartesian coordinates with x denoting the width, z the length and y the thickness. Two-dimensional motion is obtained by limiting the motion in the y direction to zero. Mirror boundary conditions are imposed on the transverse boundaries in the $\pm$ x directions and at the heated end, z = 0. The interatomic potential is that constructed by Chang[2] for α-iron. Initially, this lattice is in thermal equilibrium at a temperature T_i. Then, the first ten lattice (x-y) planes are heated quickly to an average temperature T_h and maintained at that level for the rest of the calculations. The amount of energy added to these ten planes is recorded. The classical equations of motion for the lattice atoms are solved by numerical integration, yielding the position and velocity of each atom. The average kinetic energy, potential energy, stress components and density of lattice planes are obtained as functions of time. These results show the transport of energy into the lattice.

We use the rigid mirror boundary condition in the transverse direction to prevent lateral displacement and distortion of the filament. This was necessary because we found that when periodic boundary conditions were used, as in earlier calculations, the filament would drift laterally from the equilibrium position, due to accumulation of small errors in the position and velocity of the atoms, and perhaps also due to the procedure of numerical integration. Since this motion was not uniform along the length of the filament, and since the undisturbed end was constrained to stay in place, the filament became laterally distorted and strain energy developed. Over the duration of a run (400 time units) the strain energy was such that a two fold increase in the total energy was observed. This strain energy is eliminated when the mirror boundary condition is applied.

3. CONTINUUM THEORY

Since the lattice is at a moderate initial temperature (~0.1 Θ_D, where Θ_D = Debye temperature) the mechanism of heat transfer can be expected to be diffusive. It is therefore appropriate for us to test our results against those of the continuum theory of thermal diffusion[3]. We proceed as follows:

When a time-dependent boundary temperature $T_b(t)$ is imposed on a system initially at a uniform temperature T_i, the temperature profile is given by (see ref. 3 pp. 273-4)

$$T(z,\tau) = T_i \operatorname{erf}(u) + (2/\sqrt{\pi})\int_u^\infty T_b(\tau - z^2/4\alpha u^2)\exp(-u^2)\,du \qquad (1)$$

where $u^2 = z^2/4\alpha(\tau - t)$, $\operatorname{erf}(u) = (2/\sqrt{\pi})\int_0^u \exp(-t^2)\,dt$,

α is the thermal diffusivity and z is the distance in the direction of heat flow. Although we maintain the average value of the kinetic energy in the first ten planes of the lattice at a constant value, the local kinetic temperature of the tenth (boundary) plane varies considerably on an atomic scale. For the diffusive calculation we need the average temperature of the boundary plane. In the present calculation, this may be approximated by three linear segments (see Fig. 1):

$$\begin{aligned} T_b(\tau) &= T_0 + C_1\tau, && 0 < \tau \leqslant \tau_1 \\ T_b(\tau) &= T_1 + C_2\tau, && \tau_1 < \tau \leqslant \tau_2 \\ T_b(\tau) &= T_2, && \tau_2 < \tau, \end{aligned} \qquad (2)$$

Substitution into Eq. 1 yields the following expression for the temperature profile:

$$\begin{aligned} T(z,\tau) = {} & T_i + [T_o - T_i + C_1\tau]F(u_o) - [T_o - T_i + (C_1 - C_2)\tau]F(u_1) \\ & + [T_2 - T_1 - C_2\tau]F(u_2) \\ & + 2\,C_1\tau[u_o F(u_o^2) - u_o \exp(-u_o^2)/\sqrt{\pi}] \\ & - 2(C_1 - C_2)(\tau - \tau_1)[u_1^2 F(u_1) - u_1 \exp(-u_1^2)/\sqrt{\pi}] \\ & - 2C_2(\tau - \tau_2)[u_2^2 F(u_2) - u_2 \exp(-u_2^2)/\sqrt{\pi}]. \end{aligned} \qquad (3)$$

where $F(u) = 1 - \operatorname{erf}(u)$, $u_o = z/2\sqrt{\alpha\tau}$,

$u_1 = z/2\sqrt{\alpha(\tau - \tau_1)}$, $u_2 = z/2\sqrt{\alpha(\tau - \tau_2)}$.

$T(z,\tau)$ can be fitted to our computed temperature profiles at one value of τ. Since the diffusive profile is given in terms of $u(=z/2\sqrt{\alpha\tau})$, the distance scale is arbitrary when α is unknown. This arbitrariness is removed by requiring that the area under the diffusive curve be equal to the total energy added to the system up to the time τ. With the value of α thus obtained, the diffusive curves at other times are obtained by appropriately scaling the distance. The area under these other diffusive curves must also be in agreement with the total energy added to the system at their respective times. If this is so, it can be concluded that the heat transfer in our system is indeed diffusive.

4. RESULTS

In Fig. 1, we show the boundary temperature as a function of time, $T_b(\tau)$. Even though we have averaged the kinetic temperature of planes 6 to 15 to obtain $T_b(\tau)$, there is still considerable fluctuation in the boundary temperature and we approximate it by the dashed curve C, as given in Eq. 2. The constants in these equations have the following values:

$$T_o = 59\ K,\ T_1 = 102\ K,\ T_2 = 115\ K,$$

$$\tau_1 = 20,\ \tau_2 = 208,\ C_1 = 2.214\ K \text{ and } C_2 = 0.0628\ K.$$

The time τ is measured in units of lattice plane spacing d divided by longitudinal sound velocity (equal to 0.264×10^{-13}s). The initial temperature of the lattice, T_i, is 44 K. These values are used in Eq. 3 to calculate the diffusive temperature profiles.

In Fig. 2 we show the kinetic temperature, density and longitudinal stress profiles in the lattice at time $\tau = 300$. Each point is the average of 10 neighboring planes. The kinetic temperature

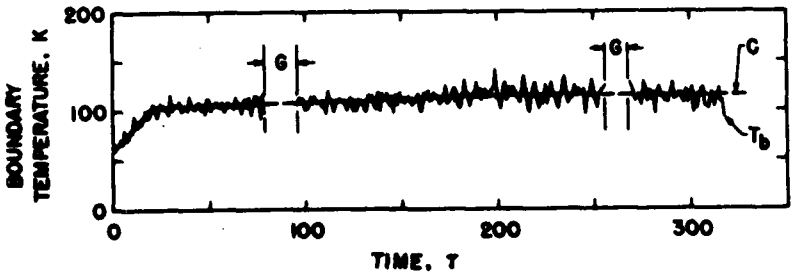

Fig.1. Boundary temperature (Kelvin) as a function of time τ (unit of $\tau = 0.264\times10^{-13}$s). T_b is the average kinetic temperature of planes 6 to 15. The boundary is at plane 10. C labels the approximate value of boundary temperature used in the continuum theory. G denotes a gap in computer output.

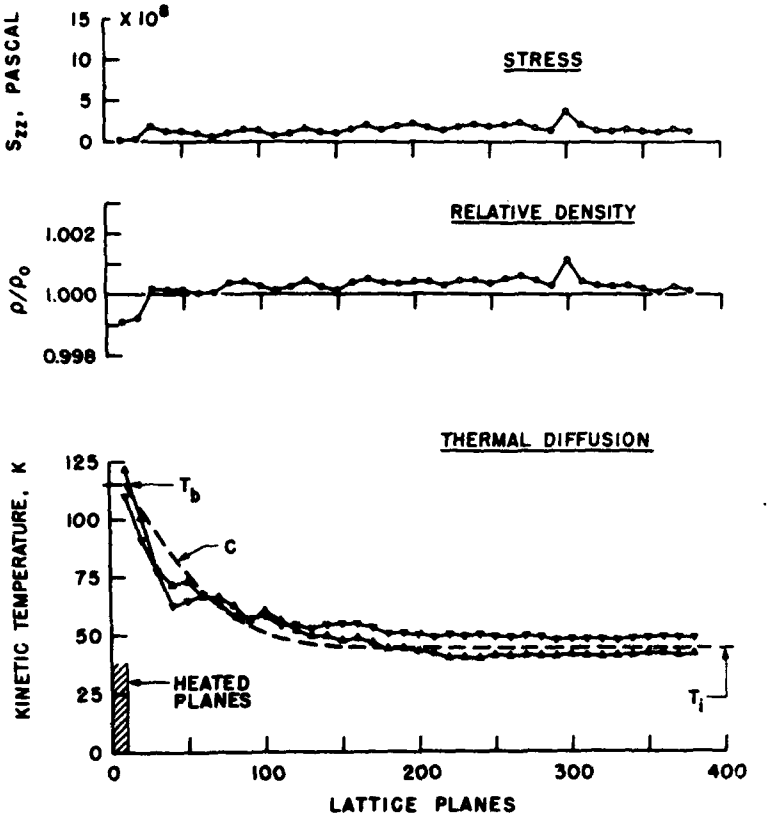

Fig.2. Kinetic temperature (Kelvin), relative density and longitudinal stress (Pascal) versus lattice plane number. Each point is the average over 10 neighboring planes. For the density ρ/ρ_o and stress, S_{zz}, $\tau = 300$; for the kinetic temperature, $\tau = 298$ (Δ) and $\tau = 303$ (∇). Continuum theory diffusive profile, C, is at $\tau = 300$ (---). $T_i = 44$ K is the uniform initial temperature of the lattice.

of a plane is defined as $m\langle V^2\rangle/2k_B$ where m is the mass of an atom, V its velocity, $\langle\cdots\rangle$ indicates the average over all atoms in the plane, and k_B is Boltzmann's constant. We plot two temperature profiles at slightly different times, $\tau = 298$ and $\tau = 303$, to show how much local fluctuation there is in the temperature. The diffusive curve, C, is calculated from Eq. 3 at $\tau = 300$. The prominent pulses in the stress and density profiles near lattice plane 300 are due to the stress and strain in the heated planes (and their image across the mirror) generated during the initial rapid heating. These pulses propagate with the longitudinal velocity of sound, as may be determined from their trajectories in a series of profiles. Although there is a slight drop in pressure near the heated

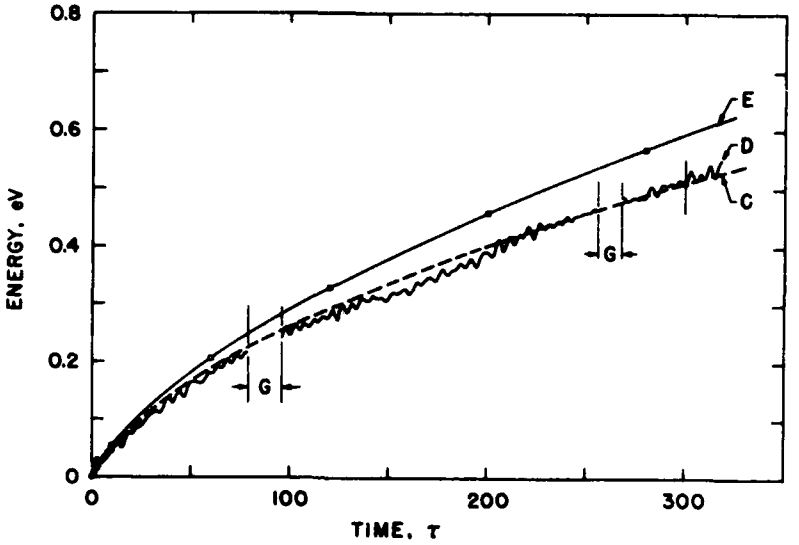

Fig.3. Energy in lattice (eV) as a function of time τ. D is the energy added to the heated planes, per filament of unit cell cross section. G denotes a gap in computer output. C is energy added to the filament as calculated by continuum theory of diffusion with $\alpha = 4\text{x}10^{-6}$ m^2 s^{-1}. E is total energy in filament minus its initial energy content.

boundary at this particular time ($\tau = 300$), our data show that both the time average and the spatial average of the stress have a constant value of $1.84\text{x}10^8$ Pascal (1.84 kilobar) behind the initial pulse. This indicates that, as expected, the stresses equilibrate with the velocity of sound. The density profile shows that the density near the heated end is definitely lower than the average density. This is clearly due to the higher temperature at the heated end and is, in our view, responsible for the observed fall of the computed temperature profile below the diffusive curve C near the heated end of the lattice. These results therefore show quite clearly the thermoelastic coupling in the lattice, a feature that is usually ignored in the continuum theory of thermal diffusion.

In Fig. 3, curve D is the energy added to the lattice at the heated end per filament of unit cell cross-section as a function of time. We calculate the diffusivity of the lattice from the diffusive curve C at $\tau = 300$ in Fig. 2, by requiring that the area under that curve be equal to the value of curve D at $\tau = 300$ in Fig. 3, as described in section 3. We obtain the following diffusivity,

$$\alpha = 4.0\text{x}10^{-6} \text{ m}^2 \text{ s}^{-1},$$

or conductivity

$$\kappa = 9.4 \text{ W m}^{-1} \text{ K}^{-1}$$

where we have used the relation

$$\kappa = \alpha \rho C_p = \alpha k_B / 2d^3.$$

We use this value of α to obtain diffusive curves at other times from Eq. 3. The areas under these curves are plotted as curve C in Fig. 3, in good agreement with the computed curve D.

The curve E shows the total energy that is actually in a filament of the lattice minus the energy that was in the lattice at uniform temperature T_i before heating. The difference between curves D and E shows the lack of energy conservation in the system due to truncation error in the numerical procedure. By the end of our run, this error amounts to about 3% of the total energy of the system.

5. DISCUSSION

The present calculation is an outgrowth of our earlier study of the propagation of a heat pulse in a lattice. One of our major objectives here is to seek additional confirmation, beyond what has been established in previous calculations, that our model is indeed realistic. Toward this end, we are able to show that the heat flow in our model is diffusive, as we expected. There is no experimental value of the lattice thermal conductivity of pure crystalline iron with which to compare our value of κ, but for the alloy Fe (99.5%) Ni (0.5%) there is a recent estimate viz., $\kappa = 28.2 \text{ W m}^{-1} \text{ K}^{-1}$ at 75 K[4]. Considering the fact that the effective interatomic potential for iron is not known at all accurately, we feel that the agreement obtained here is really quite satisfactory. In addition, our results provide a wealth of detail: for example, we see that there is thermoelastic coupling in the process of heating, and there is energy non-conservation due to the unexpected strain energy in the lattice caused by the cumulative errors in the numerical procedure. In this connection, we are able to show that when mirror boundary conditions are imposed the residual numerical error is indeed small, a few percent. There is also evidence of second sound, albeit heavily damped, propagating at this moderately high temperature. However, we shall not pursue this intriguing problem here. Further tests of the model may be devised. For example, it would be useful to investigate the effect of temperature on the lattice thermal conductivity. If the result should also prove to be reasonable, it would then be of interest to investigate thermal conductivity under conditions not easily accessible by present-day theory or

experiment, e.g., under conditions of extreme pressure. Our experience indicates, however, that the calculation of thermal diffusivity by the method of molecular dynamics is so lengthy as to be too costly and too inefficient. If the transient nature of the heat flow is not under study, then we believe that a model for steady heat flow, from which the thermal conductivity may be obtained directly[5], would be considerably more economical and more convenient to investigate than the diffusive model employed here.

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