PHYSICAL REVIEW B VOLUME 28, NUMBER 6 15 SEPTEMBER 1983

Thermal conductivity of crystals: A molecular-dynamics study of heat flow in a two-dimensional crystal

Raymond D. Mountain and Rosemary A. MacDonald
Thermophysics Division, National Bureau of Standards, Washington, D.C. 20234

(Received 16 May 1983)

We have studied steady-state heat flow in a two-dimensional crystal by the method of molecular dynamics. The model system contains 1000 particles on a triangular lattice interacting via the Lennard-Jones potential. The system is 50 unit cells long and 10 unit cells wide. We find that the thermal conductivity κ of this system is consistent with $1/T$ behavior as expected when phonon-phonon scattering is the dominant mechanism for thermal resistance. We have also carried out similar calculations for three-dimensional Lennard-Jones systems in both fluid and crystalline configurations. The results for the fluid were in good agreement with earlier calculations but for the fcc solid system, 16 unit cells in length, κ was independent of temperature. We determined that boundary scattering was the dominant resistive mechanism in this case. To escape the boundary-limited regime, the length of the three-dimensional crystal needs to be increased by at least a factor of 3. It is feasible to simulate a system of this size with the use of modern computers.

I. INTRODUCTION

In this paper we report the results of a molecular-dynamics study of heat flow in a fully dynamical, two-dimensional, crystalline lattice. This is in contrast to the first studies of nonequilibrium properties of crystalline solids, performed in the late sixties, which were devoted to steady-state studies of heat flow in spring-lattice models.[1-3] There has been little progress in this area of research as most studies have been limited to one-dimensional systems with the emphasis on determining whether or not Fourier's law is obeyed for such systems. The testing of the effect of various boundary conditions on the results has been one of the major topics of investigation. These studies have been limited to unrealistic interactions such as harmonic potentials, hard rod, or square-well interactions that lend themselves to analytic treatment. The ensuing difficulties in establishing temperature gradients in these model systems and the nonphysical results obtained have dominated the literature of this subject.[4-7] The only work to date that has given a reasonable representation of heat transport in a crystal is the molecular-dynamical study by MacDonald and Tsai[8] of the thermal diffusivity in a two-dimensional lattice. They studied the transient thermal response of a system interacting via a pair potential that had been fitted to the elastic properties of iron.[9] Another two-dimensional study considered only a harmonic lattice,[10] so thermalization was not possible.

There has been considerably greater progress reported with thermal transport in liquids. The molecular-dynamics method has been used to good effect in obtaining the time-averaged atomic quantities and their fluctuations that are needed for the thermal conductivity.[11-15] It now seems timely to examine thermal conduction in the crystalline state, building on the experience gained with the molecular-dynamical treatment of equilibrium properties of solids.[16,17]

There are several reasons for selecting the thermal conductivity for study. Firstly, the thermal transport properties are of obvious interest for high-temperature materials and for this regime, lattice-dynamical perturbation theory is probably inadequate. Secondly, the density dependence of the thermal conductivity has received very little attention[18] and this can be studied readily by molecular dynamics. Thirdly, defects are an important feature of crystals at high temperatures and there is no theoretical treatment of their motion under thermal gradients. One of the objectives of this study is to provide the basis for further, three-dimensional investigations of heat flow in solids. In particular, we show that it is feasible to simulate systems larger than the mean free path of the heat-carrying phonons.

This paper is organized in the following way. In Sec. II we describe the molecular-dynamics techniques we have used and we discuss the potential, the boundary conditions, and the stabilization procedures essential to the establishment of a steady state.

In Sec. III, we present the results that have been obtained for the two-dimensional Lennard-Jones crystal, together with some liquid-state results that served as a check on our method of calculation. We also comment on some problems which arose in our initial attempt to study a three-dimensional crystal and indicate the sort of problems which will be encountered in the simulation of heat flow in a three-dimensional crystal.

II. MOLECULAR DYNAMICS

The molecular-dynamics simulations reported in this paper were carried out using the Beeman algorithm[19] to integrate the equations of motion for N particles interacting via the Lennard-Jones pair potential,

$$\phi(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1}$$

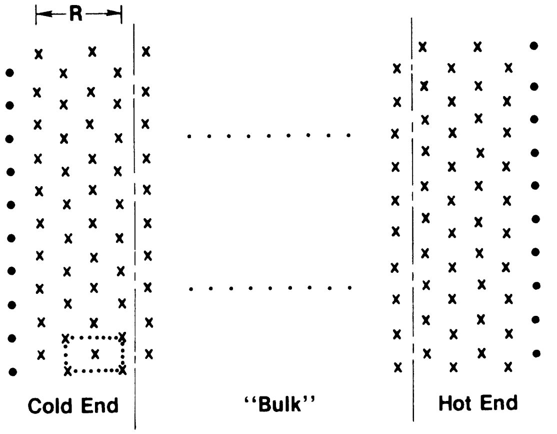

FIG. 1. The two-dimensional Lennard-Jones crystal has the triangular-lattice structure illustrated here. The system studied consisted of 10×50 unit cells (×), of which 10 unit cells at each end are explicitly shown. Two lattice planes with 10 particles each, denoted by solid circles, serve to constrain the crystal. The two rows of small dots represent the missing 480 unit cells.

Lengths are measured in units of σ and energies are measured in units of ϵ. The time is measured in units of $\tau=(m\sigma^2/\epsilon)^{1/2}$ where m is the mass of a Lennard-Jones particle. The equations of motion were integrated using a time increment of 0.01τ. The potential was truncated at $r=2.8\sigma$.

The boundary conditions used to obtain a steady, nonequilibrium state for a thermal-conductivity determination were imposed as described below. The objective is the establishment of a stable, linear temperature profile so that the thermal conductivity κ may be obtained using Fourier's law of heat flow,

$$\vec{J}=-\kappa\,\mathrm{grad}T\ . \tag{2}$$

The heat-current density $\vec{J}$ can be determined from the microscopic expression, given in Eq. (3) below, or by determining the amount of energy entering at the hot end and exiting at the cold end of the system. Both methods were used in these calculations. Agreement between the results of the two methods is a necessary condition for determining that a stationary state has been established.

The microscopic expression for the Cartesian components of the heat current is[20]

$$J^{\alpha}=\frac{1}{V}\left[\sum_j E_j v_j^{\alpha}-\tfrac{1}{4}\sum_j\sum_{k\,(\neq j)}(v_j^{\alpha}+v_j^{\beta})\frac{r_{jk}^{\alpha}r_{jk}^{\beta}}{r_{jk}}\,\frac{\partial\phi}{\partial r_{jk}}\right], \tag{3}$$

where $\alpha,\beta=x,y,z$ and the summation convention on β is assumed. E_j is the energy of particle j, v_j its velocity, r_{jk} is the distance between particles j and k, and V is the volume (area, in two dimensions) of the system.

The two-dimensional system was taken to consist of $N=1000$ particles initially located on a triangular lattice as shown in Fig. 1. The lattice was specified to be 10 unit cells wide (two particles per unit cell) and 50 unit cells long. Periodic boundary conditions were imposed in the short dimension which is transverse to the heat current. The ends of the lattice in the long dimension were stabilized by introducing an additional line of particles at each end (solid circles in Fig. 1) which are fixed in position at lattice sites and which interact with the other particles through the Lennard-Jones interaction.

The temperature gradient was introduced by requiring that a set of particles at the right end of the lattice have an average kinetic energy greater than that of a corresponding set of particles at the left end of the lattice. These sets of reservoir particles were defined as follows. A coarse grid of 25 layers was superimposed on the system. The particles lying in the leftmost layer constitute the low-temperature reservoir and the particles lying in the rightmost layer constitute the high-temperature reservoir. A major advantage of this reservoir procedure is that the resulting temperature gradient can be specified in advance, something that could not be done in the earlier work on one-dimensional lattices.[1–7] This coarse grid was also used to determine the spatial variation of the temperature, density, stress, and heat current in the system.

The determination of the thermal conductivity required first the establishment of a steady state. This was done by scaling, at each time step, the momenta of the particles lying in the right-reservoir layer and in the left-reservoir layer so that the desired temperature difference was maintained between the ends of the system. It is important that the net momentum of the layer not change as a result of rescaling momenta. This can be achieved by first adjusting the total momentum of the layer to be zero, next rescaling momenta by the desired amount, and then restoring the original net momentum to the layer. Failure to follow this procedure can lead to uncontrolled heating of the system via the impulse imparted to the system. Once a linear temperature profile, as determined by averaging over several thousand time steps, had been established, the stationarity of the system was checked using three criteria. First, the heat current in the direction of the temperature gradient should be uniform. Second, the heat current transverse to the temperature gradient should be small relative to the longitudinal current. Ideally the transverse current should be zero; in practice the best that could be obtained for the length of runs made in this study, was a small value (10–20 % of the longitudinal current) for each layer, with a distribution of + and − signs. The average of the transverse current over layers 2–24 is less than 10% of the longitudinal current. Third, the heat current determined directly should agree with the value deduced from the energy supplied to the hot end and the energy removed from the cold end.

Once a stationary system had been developed, a production run of 10 000 time steps was made. The thermal conductivity was determined from the ratio of the heat current and the temperature gradient. The temperature gradient was determined to be the difference between the temperatures of the 24th and 2nd layers divided by the center-to-center separation of those layers. In practice this ratio was indistinguishable from the slope of the temperature-position profile.

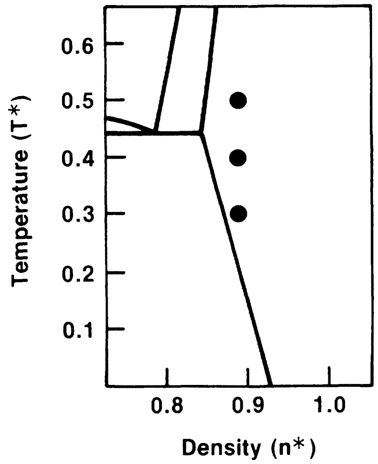

FIG. 2. A portion of the phase diagram for the two-dimensional Lennard-Jones system as discussed in Ref. 21. The solid circles locate the states studied in this work.

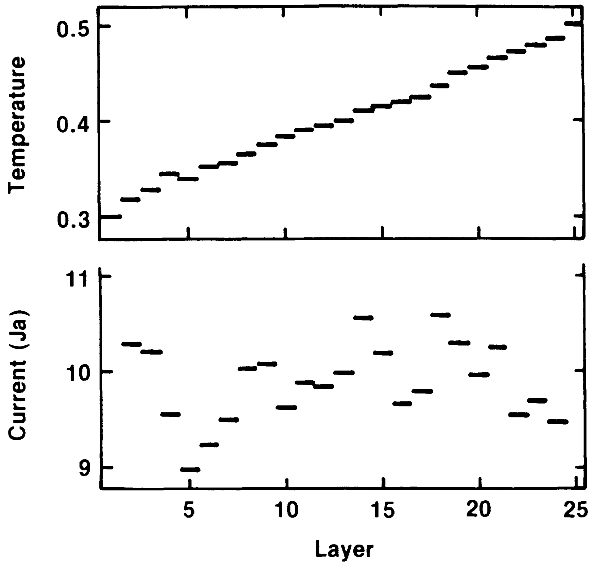

FIG. 3. Time-averaged temperature and heat current for $T_m^*=0.4$ as a function of the coarse-mesh-layer position in the crystal. The current is Ja, the heat-current density times a, the area of a layer. Note that the current for layers 1 and 25 is not shown. This is because its value is dominated by boundary effects.

Some simulations of three-dimensional systems were also made. The boundary conditions at the hot and cold ends of these systems were mirror-image conditions with the requirement that the reservoir layers were at least as thick as the range of the pair potential. In this way, the major effects of the boundary conditions should be confined to the reservoir region, at least for fluid systems. This approach works well for fluids in that no boundary layer effects, such as those found when stochastic boundary conditions are imposed,[13] were observed. This indicates that heat transport in a liquid is diffusive even on the molecular level.

Crystals are another matter entirely. Heat is carried by the phonons in an insulating crystal and the phonon mean free path determines the length scale over which boundary conditions can influence the transport of heat. A number of variants of mirror boundary conditions were tried in an attempt to minimize the mechanical mismatch between the system and the reservoirs. None of our efforts with either a 500-particle, or a 1024-particle three-dimensional crystalline system were successful as the thermal resistance was always dominated by boundary scattering. It was for this reason that our effort was concentrated on a two-dimensional system where we have estimated the mean free path of the longitudinal phonons at the temperatures of interest to be on the order of 10 unit cells. This estimate is based on the decay of the intermediate scattering function[16] for an equilibrium two-dimensional crystal. Thus with a manageable number of particles, the size of the system could greatly exceed the phonon mean free path.

TABLE I. Thermal conductivity κ of the two-dimensional Lennard-Jones crystal at density $n^*=0.9$. T_m^* is the midpoint temperature for the crystal. $\langle J_z \rangle$ is the average current density in the direction of the gradient. κ is given in units of $k_B\tau^{-1}$. The uncertainty in κ is on the order of 10–15 %.

T_m^*	κ	κT_m^*	$\langle J_z \rangle$
0.3	182	54.6	0.39
0.4	128	51.2	0.27
0.5	117	58.5	0.26

III. RESULTS

The phase diagram for the two-dimensional Lennard-Jones system has been discussed by van Swol *et al.*[21] A portion of the temperature-density diagram is shown in Fig. 2 and we indicate where our heat-flow simulations were made. We report temperatures and densities in the usual reduced form $T^*=k_BT/\epsilon$ and $n^*=N\sigma^2/A$, respectively, where k_B is the Boltzmann constant and A is the area of the system. Three states with mean temperature $T_m^*=0.3$, 0.4, and 0.5 were studied. In each case the cold reservoir was maintained at $T_m^*-0.1$ and the hot reservoir was maintained at $T_m^*+0.1$. The simulations were performed as described in the previous section.

The results are summarized in Table I. As an illustration of how these results were obtained, we show in Fig. 3 the temperature and heat-current profiles for the $T_m^*=0.4$ case. The scatter in the values indicates the uncertainties associated with the heat current (5–10 %) and the temperature gradient (5%), so the uncertainty in κ is on the order of 10–15 %. This is the level of uncertainty reported in Ref. 14. The κT values are constant to within 10%, so that within the sizable uncertainties involved, the thermal conductivity is consistent with $1/T$ behavior, the expected result when phonon-phonon scattering is the dominant mechanism for thermal resistance.[22]

Finally, let us briefly consider the simulation of heat flow in a three-dimensional system. We performed a simulation of heat flow in a 500-particle Lennard-Jones liquid system with density $n^*=0.85$ and temperature $T^*=0.806$ so that we could check our results against earlier liquid simulations. Our value for the thermal conductivity agrees closely with that reported in Ref. 14. We also carried out heat-flow simulations for the Lennard-Jones crystal, an fcc lattice, 16 unit cells in length. Unlike the results for the two-dimensional case reported above, the thermal conductivities were found to be independent of temperature, indicating that the scattering was boundary limited. An equilibrium determination of the intermediate scattering function[16] revealed that the mean free path for longitudinal phonons was greater than the size of the system we were studying. This means that boundary scattering will be a significant source of thermal resistance for such a system. In order to reduce boundary effects and have phonon-phonon scattering as the dominant source of thermal resistance in three dimensions, it will be necessary to simulate systems that are several times as long as the present one, i.e., containing several thousand particles. This is within the capabilities of modern computers, although it is not a minor task.

---

[1] Z. Rieder, J. L. Lebowitz, and E. Lieb, J. Math. Phys. 8, 1073 (1967).

[2] D. N. Payton, M. Rich, and W. M. Visscher, Phys. Rev. 160, 706 (1967).

[3] E. A. Jackson, J. R. Pasta, and J. F. Waters, J. Comput. Phys. 2, 207 (1968).

[4] H. Matsuda and K. Ishii, Prog. Theor. Phys. Suppl. 45, 56 (1970).

[5] H. Nakazawa, Prog. Theor. Phys. Suppl. 45, 231 (1970).

[6] W. M. Visscher, Prog. Theor. Phys. 46, 729 (1971); Methods Comput. Phys. 15, 371 (1976).

[7] E. A. Jackson, Rocky Mt. Math. J. 8, 125 (1978).

[8] R. A. MacDonald and D. H. Tsai, in *Thermal Conductivity—14,* Proceedings of the Fourteenth International Conference on Thermal Conductivity, Storrs, Connecticut, 1975, edited by P. G. Klemens and T. K. Chu (Plenum, New York, 1976), p. 145; Phys. Rep. 46, 1 (1978).

[9] D. H. Tsai and R. A. MacDonald, Trans. Am. Crystallog. Assoc. 7, 107 (1971).

[10] A. J. O'Connor and J. L. Lebowitz, J. Math. Phys. 15, 692 (1974).

[11] W. T. Ashurst, in *Advances in Thermal Conductivity,* Proceedings of the Thirteenth International Conference on Thermal Conductivity, Rolla, Missouri, 1973, edited by R. L. Reisbig and H. J. Sauer, Jr. (University of Missouri, Rolla, 1974), p. 89.

[12] G. Ciccotti, G. Jacucci, and I. R. McDonald, J. Phys. C 11, L509 (1978).

[13] G. Ciccotti and A. Tenebaum, J. Stat. Phys. 23, 767 (1980).

[14] A. Tenebaum, G. Ciccotti, and R. Gallico, Phys. Rev. A 25, 2778 (1981).

[15] D. J. Evans, Phys. Lett. 91A, 457 (1982).

[16] J. P. Hansen and M. L. Klein, Phys. Rev. B 13, 878 (1976).

[17] R. C. Shukla and R. D. Mountain, Phys. Rev. B 25, 3649 (1982).

[18] D. N. Batchelder, in *Rare Gas Solids II,* edited by M. L. Klein and J. A. Venables (Academic, New York, 1977), pp. 883–920.

[19] D. Beeman, J. Comput. Phys. 20, 130 (1976).

[20] P. Schofield, Proc. Phys. Soc. 88, 149 (1966).

[21] F. van Swol, L. V. Woodcock, and J. N. Cape, J. Chem. Phys. 73, 913 (1980).

[22] P. G. Klemens, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7, and references contained therein.