

Thermal conductivity of the Lennard-Jones fluid

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We use the Evans method [Phys. Lett. **91A**, 457 (1982) to simulate heat flow in the Lennard-Jones fluid. With use of the standard Lennard-Jones representation of argon, the results are in broad agreement with experimental argon data except in a small region close to the critical point. The results indicate that away from phase boundaries there is little N dependence of the computed results. Close to the critical point the computed effective thermal conductivity is a nonmonotonic function of the external field. The long-time tail of the heat flux autocorrelation function is somewhat larger than mode-coupling predictions.

I. INTRODUCTION

At present the only known homogeneous method for simulating heat flow in a periodic system is due to Evans.¹ In this method a fictitious external field \mathbf{F} essentially replaces the role played in experiment by the temperature gradient ∇T . Linear-response theory is then used to prove that in the linear regime the ratio of the heat flux \mathbf{J}_Q to the external field \mathbf{F} is equal to the thermal conductivity multiplied by the absolute temperature. Consider the following equations of motion:

$$\begin{aligned} d\mathbf{q}_i/dt &= \mathbf{p}_i/m, \\ d\mathbf{p}_i/dt &= \sum_j \mathbf{F}_{ij} + (E_i - E)\mathbf{F}(t) - \sum_j \mathbf{F}_{ij}\mathbf{q}_{ij} \cdot \mathbf{F}(t) \\ &\quad + \sum_{j,k} \mathbf{F}_{jk}\mathbf{q}_{jk} \cdot \mathbf{F}(t)/2N - \alpha\mathbf{p}_i, \end{aligned} \quad (1)$$

where α , the thermostating multiplier, is

$$\alpha = \sum_i \left[\sum_j \mathbf{F}_{ij} + (E_i - E)\mathbf{F}(t) - \sum_j \mathbf{F}_{ij}\mathbf{q}_{ij} \cdot \mathbf{F}(t) + \sum_{j,k} \mathbf{F}_{jk}\mathbf{q}_{jk} \cdot \mathbf{F}(t) \right] \cdot \mathbf{p}_i / 2N \sum_i \mathbf{p}_i \cdot \mathbf{p}_i.$$

In Eq. (1), E_i is the instantaneous energy of particle i , $E = \sum_i E_i/N$, \mathbf{F}_{ij} is the force on particle i due to j , and $\mathbf{q}_{ij} = \mathbf{q}_j - \mathbf{q}_i$. It is relatively straightforward to show that if the external field is constant, then

$$\lim_{t \rightarrow 0} \mathbf{J}_Q \sim \lambda \mathbf{F} / T \quad \text{as } \mathbf{F} \rightarrow 0. \quad (2)$$

This result is proved by comparing the linear response to \mathbf{F} with the Green-Kubo expression for the thermal conductivity, λ :

$$\lambda = \frac{V}{3k_B T^2} \int_0^\infty dt \langle \mathbf{J}_Q(t) \cdot \mathbf{J}_Q(0) \rangle. \quad (3)$$

A number of points need to be made about these equations of motion. The term $\alpha\mathbf{p}_i$ is the Gaussian thermostat.^{2,3} It ensures that the temperature as measured by the kinetic energy, $\sum \mathbf{p}^2/2m (=3Nk_B T/2)$, is a constant of the motion. This means that the order of taking limits in

(2) can be interchanged without changing the result.^{3,4} This is, of course, not possible in adiabatic linear-response theory. For computer simulations the thermostat is, of course, indispensable since otherwise the heating of the system would prevent the attainment of a true steady state. Isothermal linear-response theory shows that the Gaussian thermostat is relatively benign. It leaves the formal expression for the linear response unaltered⁴ except that in the equilibrium time-correlation function (3) propagation is governed by the field-free Gaussian isothermal propagator rather than by the corresponding Newtonian propagator. We have recently proved that in the thermodynamic limit the adiabatic and isothermal equilibrium time-correlation functions are identical.^{5,6}

A second point about these equations of motion is that even in the absence of a thermostat, no Hamiltonian has been found which is capable of generating the (adiabatic) equations of motion. It can be shown that provided the adiabatic incompressibility of phase-space condition (AIF) is fulfilled, linear-response theory for Hamiltonian systems has a simple generalization to non-Hamiltonian systems.^{4,6} It is worth noting that an apparently similar set of equations due to Gillan⁷ do not satisfy AIF.^{6,8} One manifestation of this property of the Gillan equations is that in contrast to our equations (1), the Gillan equations do not conserve momentum.

A third property of our equations is that they are consistent with the periodic boundary conditions used in computer simulations. Indeed, it was the necessity of satisfying these conditions that originally lead to the abandonment of Hamiltonian forms for the dynamics.¹

Because the external field acts homogeneously the heat flux is created in the complete absence of temperature or density gradients. It is the unavoidable presence of these gradients in real heat flow that means that a straightforward simulation of heat flow between walls maintained at different temperatures is fraught with severe interpretive difficulties.^{6,9}

The price we pay for these substantial benefits is that outside the linear regime close to equilibrium, no meaning is known for the field-dependent nonlinear transport coefficient \mathbf{J}_Q/F . All that is presently known is that in the zero field limit this ratio is equal to the thermal conduc-

tivity times the absolute temperature.

In this paper we use the dynamics described by Eqs. (1) to study heat flow in the Lennard-Jones fluid. The intermolecular potential function $\Phi(q)$,

$$\Phi(q) = 4(q^{-12} - q^{-6}) \quad (4)$$

was truncated at $q=2.5$. Most of the calculations we performed for 108-particle simulations although a small number of comparisons were made for 256-particle systems to check the number dependence of the results.

II. ZERO-FREQUENCY THERMAL CONDUCTIVITY

Most previous studies of Lennard-Jones thermal conductivities have been restricted to the triple-point region.^{1,10} In this study we performed simulations for a wide range of state points. Figures 1–3 show computed thermal conductivities as a function of external field F for the critical isotherm ($T=1.35$), for a supercritical isotherm ($T=2$), and for two state points along the Lennard-Jones freezing line. Apart from the critical point simulation ($T=1.35, \rho=0.4$) the agreement with experiment is within statistical uncertainties. In general, the effective field-dependent conductivity seems to be a monotonic, virtually linear, function of the external field. If this could be established theoretically it would greatly increase our confidence in the unavoidable extrapolation to zero field to obtain the thermal conductivity. This essentially linear behavior was also seen in our earlier triple-point calculations.¹

Figure 4 shows the critical point results in more detail. It appears that at least for this state point, a linear relation between the conductivity and the field is not valid over the range of field strengths studied. Because of the well-known critical enhancement of thermal conductivity, we should not expect to be able to calculate the correct thermal conductivity for small periodic systems that are close to the critical point. We note that the disagreement

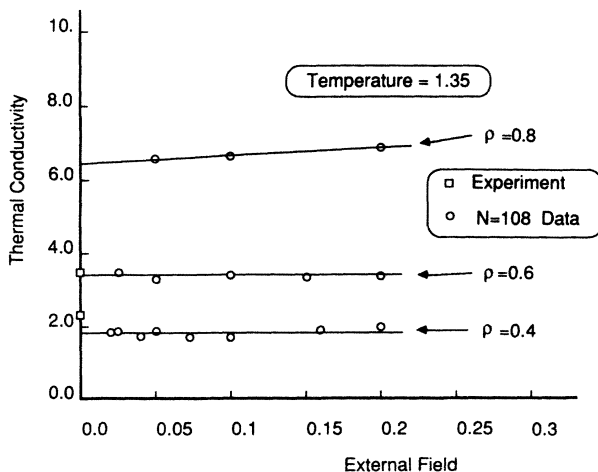


FIG. 1. Computed conductivity as a function of external field F for the critical isotherm ($T=1.35$). Except for the critical-point state, extrapolated zero-field conductivities agree with experimental thermal conductivities (Ref. 20) within estimated statistical uncertainties.

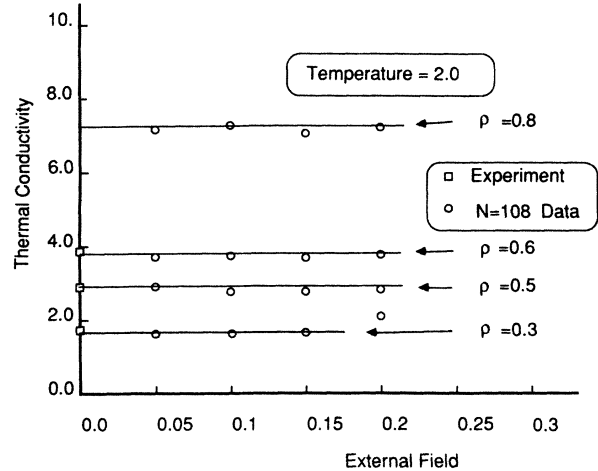


FIG. 2. Computed conductivity as a function of external field F for a supercritical isotherm ($T=2$). Except for the critical-point state, extrapolated zero-field conductivities agree with experimental thermal conductivities (Ref. 20) within estimated statistical uncertainties.

with experiment is in the expected direction, simulation being some 11% smaller than experiment.

Figure 5 shows some of our earlier triple-point data together with some new results for a 256-particle system. One immediately sees the apparently linear field dependence of the conductivity. At fields greater than 0.2 the results show no discernable N -dependence. At $F=0.2$, two conductivities are obtainable for the larger system. One of the conductivities is in excellent agreement with the 108-particle results. At the smaller field ($F=0.1$), only one conductivity is observable in the system. It is larger than the corresponding 108-particle result.

At a field of 0.2 the two different conductivities were obtained depending upon whether the state point was approached from higher or lower fields. The system thus exhibits hysteresis. We believe that for the 256-particle

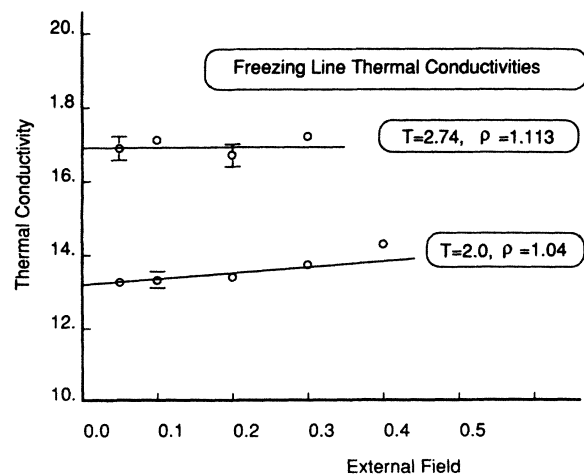


FIG. 3. Computed conductivity as a function of external field F for two state points along the Lennard-Jones freezing line. Except for the critical-point state, extrapolated zero-field conductivities agree with experimental thermal conductivities (Ref. 20) within estimated statistical uncertainties.

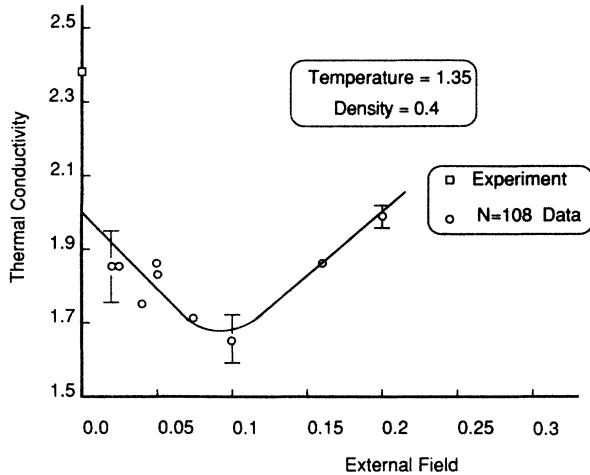


FIG. 4. Computed conductivity for the Lennard-Jones critical point ($T=1.35$, $\rho=0.4$). Note the nonmonotonic variation with field. The zero-field thermal conductivity disagrees with experiment (Ref. 20) by a statistically significant amount.

system, the equilibrium ($F=0$) phase is the solid rather than the liquid. As the field increases the system undergoes a phase transition to a (thermally conducting) liquid phase. If this hypothesis is correct it should be possible to promote the same transition by varying the temperature at constant field rather than by varying the field at constant temperature. Fixing the field at 0.1, where only one phase is stable, presumably the solid, we increased the temperature to form the thermally conducting liquid. This was observed as a sharp drop in the observed conductivity (see

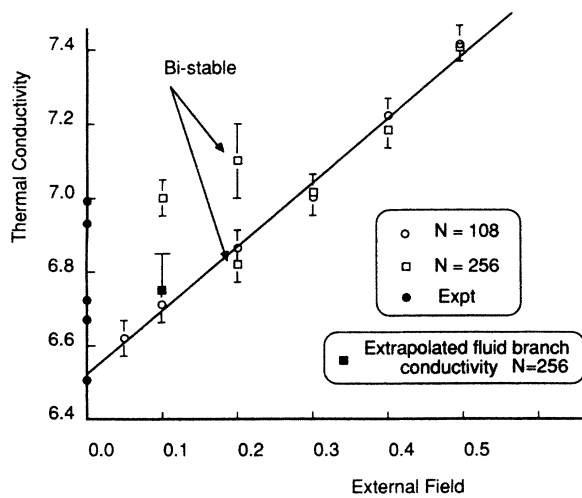


FIG. 5. Conductivity for the triple-point state. The results are shown as a function of external field and system size. At low fields the 256-particle system has an equilibrium phase which differs from that of the 108-particle system. They are presumably solid and liquid, respectively. The filled-in square shows the extrapolated liquid-phase conductivity for 256 particles at $F=0.1$ (see Fig. 6). We conclude there is no significant N dependence for the Evans method provided systems are in the same phase. The calculated results are in agreement with experimental data (Refs. 20 and 21).

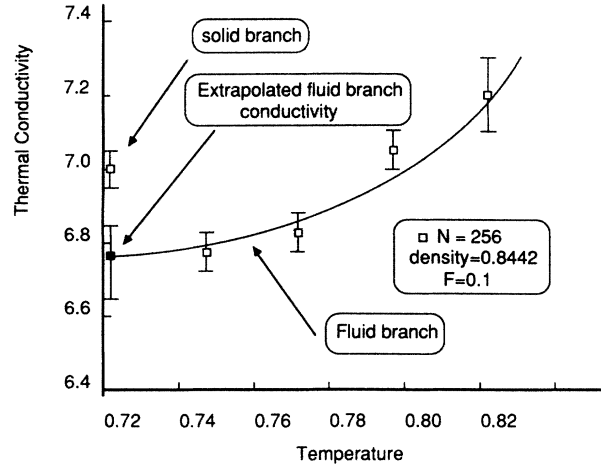


FIG. 6. For the 245-particle system, heating at $F=0.1$ melts the system, giving a conductivity which when extrapolated to the triple-point temperature agrees with the 108-particle results at that field.

Fig. 6). At a fixed field of 0.1, it can be seen that there are again apparently two stable branches with the transition occurring at a temperature in the range $0.722 < T < 0.747$. Using the high-temperature-liquid data we can extrapolate down to $T=0.722$ to obtain the estimated $F=0.1$, liquid phase, 256-particle conductivity. The result of this extrapolation is shown in Fig. 5. It is in excellent agreement with the corresponding 108-particle results and with the high-field 256-particle conductivities extrapolated to $F=0.1$.

In retrospect it was probably unfortunate to attempt the N -dependence study for a fluid close to its triple point. We conclude, however, that in the dense fluid phase there is no significant N dependence of computed conductivities for the Evans method. Of course this cannot be expected to apply in the critical point region.

The extrapolated thermal conductivity for the Lennard-Jones triple point agrees well with the argon experimental results. However, we can see from Fig. 5 that there is considerable uncertainty in the experimental results. In fact, it would appear from our simulations that it should be possible to calculate the argon thermal conductivity more accurately than it can be measured experimentally. Of course, one would have to use a more accurate representation of the argon intermolecular potential than that provided by the Lennard-Jones representation.

III. FREQUENCY-DEPENDENT THERMAL CONDUCTIVITY

If we chose an external field which has a sinusoidal time dependence, we can, of course, calculate the frequency-dependent conductivity $\lambda(\omega)$. It is well known that

$$\lambda(\omega) = \frac{V}{3k_B T^2} \int_0^\infty dt e^{i\omega t} \langle \mathbf{J}_Q(t) \cdot \mathbf{J}_Q(0) \rangle. \quad (5)$$

Equation (5) shows that the complex frequency-dependent thermal conductivity gives us the Fourier-

Laplace transform of the heat-flux autocorrelation function at equilibrium.

In the past we have used the same technique to study the stress autocorrelation function using nonequilibrium molecular dynamics simulations of viscous flow.^{11,12} As is now well known^{11,13} the equilibrium stress autocorrelation function seems to be dominated at long times by what have become known as “enhanced long-time tails.” In three dimensions these tails appear to decay as $t^{-3/2}$ giving rise at low frequencies to a square-root cusp in the real and imaginary parts of the frequency-dependent viscosity. In two dimensions these tails appear to decay as t^{-1} , leading to the possible divergence of viscosity in two dimensions. In a recent paper we have presented simulation data which suggest that in two dimensions at sufficiently long times and low strain rates, planar shear flow itself becomes unstable, thus screening the two-dimensional divergence.¹⁴

One of the interesting aspects of these tails is that the functional time dependences observed in computer simulations agree with those predicted by mode-coupling theory. This is the case for both the frequency and strain-rate dependences, in two, three, and even four dimensions. The amplitudes of the observed tails are, however, orders of magnitude larger than theoretical predictions. Further, the theoretical dependence of tail amplitudes upon temperature and density are also in disagreement with the simulation results. Although bulk viscosity has been studied less extensively it too seems to exhibit an enhanced long-time tail.¹⁵ It therefore seemed of interest to perform similar calculations for thermal conductivity to ascertain whether enhanced tails are confined to viscosity and related transport coefficients.¹⁶

Figure 7 shows the complex frequency-dependent thermal conductivity as a function of the square root of the frequency. Like viscosity it reveals a monotonic decrease in the real part of the conductivity with increasing frequency. However, unlike viscosity, Fig. 7 shows a slight shoulder at a frequency of approximately 2. It is well known that at low frequencies the imaginary part of the transport coefficient is subject to larger statistical uncertainties than the corresponding real part.¹¹ This is partly explained by the fact that, relative to the imaginary branch, there is a greater range of frequencies over which the asymptotic ($\omega \rightarrow 0$) dependence is observable in the real part of the spectrum. This can be clearly seen in Figs. 7 and 8. The real part of the low-frequency data is consistent with the behavior

$$\text{Re}[\lambda(\omega)] = (1.9 \pm 0.1) - (0.3 \pm 0.05)\omega^{1/2}.$$

Mode-coupling theory¹⁷ predicts that rather than 0.3, the coefficient of the square-root cusp should be approximately 0.05 ± 0.01 . This estimate was based upon the known properties of the 108-particle Lennard-Jones fluid rather than upon the experimental properties of argon. The main uncertainty in the calculation of the theoretical mode-coupling amplitude is the unknown bulk viscosity. We have assumed that it is equal to the shear viscosity. The amplitude is not sensitive to the precise value of the bulk viscosity. We use the Lennard-Jones properties rather than those of argon to try to avoid difficulties due to

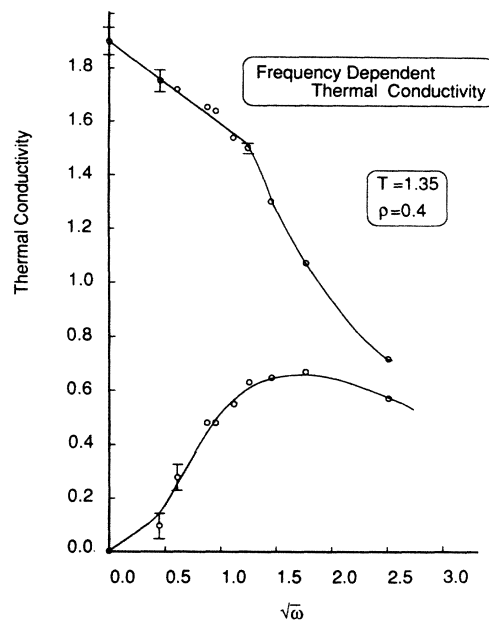


FIG. 7. Real and imaginary parts of the critical-point, frequency-dependent thermal conductivity. The field amplitude used in these calculations was 0.1. It was found that there is negligible field dependence of the results at nonzero frequencies. It appears that at low frequencies the results are consistent with a square-root variation with frequency. The observed amplitude appears to be about an order of magnitude larger than mode-coupling predictions.

the small system size restricting the critical behavior that would be found in real argon. The actual critical point of the 2.5 cutoff Lennard-Jones fluid is not known with great accuracy. It is highly dependent upon details of system size and cutoff distances and procedures.

Although the data shown in Fig. 7 are not of as high

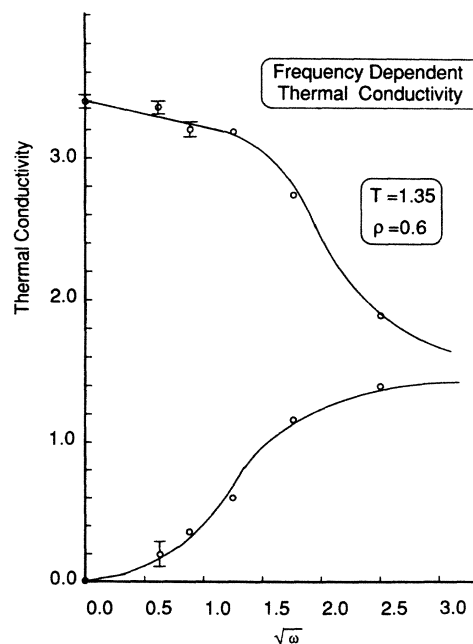


FIG. 8. Similar data to Fig. 7 except that the density has been increased to 0.6.

quality as the corresponding shear-viscosity data, it appears that mode-coupling amplitude may be as much as a factor of 6 times smaller than the observed amplitude. Figure 8 shows the results at a slightly higher density on the critical isotherm. Here the long-time-tail amplitude seems to be much reduced and it is much more difficult to determine with any accuracy. Our tentative figures at $T = 1.35$, $\rho = 0.6$ are

$$\text{Re}[\lambda(\omega)] = (3.4 \pm 0.1) - (0.16 \pm 0.1)\omega^{1/2}.$$

The mode-coupling amplitude at this state point is approximately 0.03.

IV. CONCLUSION

We have shown that the Lennard-Jones thermal conductivity calculated using the Evans algorithm is in good agreement with experimental argon thermal conductivities over a broad range of temperatures and densities. It in fact appears possible to use accurate potential functions to calculate inert-gas thermal conductivities more accurately than they can be measured experimentally, at least in regions of the phase diagram that are not close to the critical point.

Our extrapolated triple-point thermal conductivity is in excellent agreement with very recent calculations for the same system carried out by Paolini, Ciccotti, and Massobrio.¹⁸ The chief difference between our calculations and theirs is that Paolini, Ciccotti, and Massobrio use an im-

pulse field F in Eq. (1) rather than the steady field used in this work. Their calculations also reveal a negligible dependence of the computed results upon the system size, provided $N \geq 108$.

Away from the critical region it seems that the field-dependent conductivity is essentially a linear function of the applied external field. Near the critical point it is probable that long-time-tail effects are responsible for the nonmonotonic variation of the conductivity with respect to the external field. It also seems possible that mode-coupling theories underestimate the amplitude of these long-time tails. The discrepancy seems, however, to be much smaller than is the case for shear or bulk viscosity.

Provided one is not too close to a phase boundary there seems to be little N dependence in the computed results. This conclusion is supported by recent calculations that we have performed on thermal conductivity and diffusion in binary mixtures.¹⁹

Note added in proof. We have recently proved that despite the violation of momentum conservation and $A\Gamma$, the Gillan algorithm is correct [MacGowan and Evans (unpublished)].

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