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Lennard-Jones triple-point conductivity via weak external fields: Additional calculations

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Two recent studies of Lennard-Jones liquid-phase triple-point heat conductivity suggested very different nonlinear dependences of conductivity on field strength. This difference appeared to be paradoxical because the two calculations used very similar driving forces to generate heat flows. Here we analyze two sets of model calculations parallel to the Lennard-Jones work. The calculations describe a simple relaxation-time model for field-induced diffusive flow in a low-density gas of two hard disks. The nonlinearities found in the simple model suggest that the difference between the two Lennard-Jones conductivity calculations mainly reflects a difference in the comparable strengths of the currents studied.

I. MOTIVATION

In a series of nonequilibrium molecular-dynamics simulations Massobrio and Ciccotti[1] found a heat conductivity independent of field strength. In these calculations the strength of the driving field was varied over more than six decades. In an independent study, Evans[2] found a heat conductivity which varied linearly with field strength, for the same force law and thermodynamic state. Evans's calculations spanned one decade in field strength.

The two sets of data, shown in Fig. 2 of Ref. 1, seem to be contradictory. But the two calculations are different in detail. Evans's steady-current calculations used a constant external driving field. Massobrio and Ciccotti used a relatively weak impulsive delta-function field and followed the decay of the resulting heat current. Because a delta-function field seems more abrupt than a steadily applied field, it seems natural to expect somewhat larger nonlinear effects in the delta-function case, for comparable field strengths. Comparability of impulsive and steady fields involves the choice of a characteristic time. Massobrio and Ciccotti used the molecular-dynamics time step in comparing the fields. The model calculations described here suggest that a correlation time of the order of the collision time is a better choice. The model calculations suggest that nonlinear effects similar to those seen by Evans could also be observed with impulsive fields, but at field strengths some 20—40 times larger than those used by Massobrio and Ciccotti.

II. MODEL

We seek to clarify the apparent contradiction between the steady-[2] and impulsive-field[1] results by analyzing a simple two-particle model for field-driven diffusion taken from kinetic theory. The model we study here is an initially isoenergetic ensemble of two-body systems with no center-of-mass motion. Every system in the ensemble obeys the same equations of motion, but with different initial conditions. We follow only the average behavior of "particle 1," as described by the one-particle probability density function $f(r,p,t)$. It is assumed that the density function for our ensemble is described by the relaxation-time Boltzmann equation

$$(\partial f/\partial t)+(\partial/\partial r)(f\dot{r})+(\partial/\partial p)(f\dot{p})=(\partial f/\partial t)_{\text{collisions}} ,$$
$$(\partial f/\partial t)_{\text{collisions}}=(f_0-f)/\tau . \quad (1)$$

We are interested in the spatially homogeneous case with $f(r,p,t)=f(p,t)$, so that the spatial-gradient term in the Boltzmann equation $(\partial/\partial r)(f\dot{r})$ vanishes. We denote the field-free equilibrium distribution by f_0 and the two-particle collision rate, which is proportional to the momentum p, by $1/\tau(p)$. The linear collision term $(f_0-f)/\tau$, is exact for two hard spheres, with momenta $\pm p$, because hard-sphere scattering is isotropic in the center-of-mass frame appropriate to such a two-body system. Because hard disks lead to very similar results, with less work, we describe only the hard-disk case here. Both diffusion[3] and shear viscosity[4,5] have been studied for this model, but with attention focused primarily on understanding steady-state flows.

We will consider two different forms of accelerating field: (i) a constant field E producing a momentum change Edt during the infinitesimal interval dt, and (ii) an impulsive delta-function field $E\Delta t$, producing a momentum change $E\Delta t$ during any interval that includes the time zero. The additional factor of Δt in the impulsive-field strength is required for dimensional consistency.

The possibility of momentum-dependent non-Hamiltonian constraint forces is included in (1). Such "thermostat forces," "linear" in the momenta,[3-5] are used here to maintain a nonequilibrium steady state with fixed kinetic energy. We put quotes around "linear" as a reminder that the friction coefficient multiplying the momentum is itself a function of the momenta. Thus the equation of motion is nonlinear.

An external field accelerates one particle, "particle 1," in each system to the right and the other particle, "particle 2," to the left. Thus the total momentum p_1+p_2 is zero, and is unchanged by the driving and constraint forces. The symmetry of the two-particle problem allows us to infer the behavior of particle 2 from that of particle 1. Accordingly, we consider in what follows that the

Boltzmann equation solution $f(p,t)$, normalized to unity, gives the probability density for particle 1 in momentum space. The current $\langle p \rangle = \int f p \, dp$ likewise is the one-particle current due to particle 1.

Massobrio and Ciccotti used a form of linear-response theory[6] as the basis of their flow simulation. In linear-response theory, transport coefficients can be measured in a variety of ways, using delta function, step function, or sinusoidal driving forces, with or without constraint forces used as thermostats. In the nonlinear case there is neither a general proof nor a reasonable expectation that these various field-dependent nonlinear transport coefficients will coincide. In Sec. III we compare three different nonlinear mobilities—or diffusion coefficients—obtained by solving (1) with both steady and impulsive accelerating fields.

III. RESULTS

We consider the steady-state solution of (1) as well as two nonsteady solutions. The steady-state diffusion coefficient, which gives the current resulting from a constant field of strength E, has already been calculated[3] from the Boltzmann equation (1) for this system. In the nonsteady problems the two hard disks are accelerated by an impulsive delta-function external field $E\Delta t$. This field drives particle 1 to the right and particle 2 to the left. In the "adiabatic" case each system is allowed to heat up, or cool off, as a result of this interaction with the field. In the "isothermal" case an additional thermostat constraint force $F_c = -\zeta p$, extracts or supplies kinetic energy at the same rate that energy is gained from or lost to the field. The same kinetic model which underlies the Boltzmann equation, a low-density gas with no correlations between successive collisions, and with random velocity directions after collisions, is used here. For more details see Refs. 3–5 and the Appendix.

In all three cases, we consider an initial ensemble of two-body systems with fixed center-of-mass momentum $(p_1+p_2=0)$ and fixed kinetic energy $kT=(p_1^2+p_2^2)/2m$. Initially, the momentum distribution in the ensemble is uniform over the allowed states in momentum space.

In Table I we compare three different nonlinear diffusion coefficients: (i) the steady-state coefficient from Ref. 3, (ii) the adiabatic coefficient obtained with a delta-function field, and (iii) the isothermal coefficient obtained with field (ii) and a thermostat.

The three cases have been compared by expressing the field strength in terms of the initial momentum p_0 and collision rate $1/\tau_0$. $E\tau_0/p_0$ and $E\Delta t/p_0$ are dimensionless, and appear in column one of Table I. It must be emphasized that the comparison requires choosing a time relating the strength of the steady and impulsive fields. In the two-particle case the natural time to choose is the collision time τ_0. We use $2\tau_0$ in the isothermal case simply because the resulting mobilities correspond better with that choice.

The mobilities, ratios of current to field, have likewise been compared in dimensionless form. In the linear regime the steady-field response $I/\tau_0 E$, and the impulsive-field response $\int I dt/\tau_0 E\Delta t$, match the value $\frac{1}{2}$ from Ref. 3. In the nonlinear case this dimensionless mobility falls below the linear value. It is interesting to see that the trends of the mobilities, for the fields shown in Table I, are similar.

TABLE I. Mobilities as a function of field strength for two hard disks according to the three methods outlined in the text. The steady-state values are taken from Ref. 3. The steady-state calculations use a field E. The delta-function calculations use an impulsive field $E\Delta t$ applied at the initial time. I is the "one-particle current," $\langle p_1 \rangle = -\langle p_2 \rangle$. The energy of the two-body system is p_0^2/m in the steady and isothermal cases. In the adiabatic case the energy increases to an average value of p^2/m. For the comparison given in the table the dimensionless constant C has been chosen equal to one in the adiabatic case and two in the isothermal case.

$E\tau_0/p_0$ or $E\Delta t/Cp_0$	$I/\tau E$ Steady	$\int I dt/\tau E\Delta t$ Adiabatic	Isothermal
0.0	0.5000	0.5000	0.5000
0.1	0.4975	0.4981	0.4983
0.2	0.4907	0.4928	0.4934
0.3	0.481	0.4845	0.4855
0.4	0.468	0.4741	0.4749
0.5	0.455	0.4627	0.4621

This comparison strongly suggests that the steady and impulsive Lennard-Jones conductivities measured by Evans,[2] Massobrio, and Ciccotti[1] should also be compared by choosing an appropriate "collision time" or "correlation time." Although this time is not a precise concept an estimate can be based on the time required for the current correlation function to fall to a value of $1/e$, about $0.11(m\sigma^2/\epsilon)^{1/2}$ in Lennard-Jones units, or on the time integral of the correlation function, about $0.14(m\sigma^2/\epsilon)^{1/2}$. These times are about 30 times larger than the value $h=0.0045(m\sigma^2/\epsilon)^{1/2}$ used to compare the data in Fig. 2 of Ref. 1.

Accordingly, we expect that impulsive Lennard-Jones conductivities at fields some 30 times higher than those used by Massobrio and Ciccotti may well reveal nonlinearities similar to those found by Evans. This question is being investigated.[7]

APPENDIX

Here we outline the numerical calculation of the impulsive-field mobilities given in Table I. In carrying these calculations out, it is convenient to average over the before-field probability density, with all momentum directions, corresponding to $0 \le \theta \le 2\pi$, equally weighted. In the adiabatic case (ii) there is no thermostat force. The momentum p after applying the field is $p=(p_0\cos\theta + E\Delta t, p_0 \sin\theta)=(p_x,p_y)$. The post-field temperature $\langle p^2/mk \rangle$ is equal to $T_0+(E\Delta t)^2/mk$. The time integral of the current becomes

$$\int_0^\infty I dt = \int_0^\infty dt \int dp\, f(p,t) p = (1/2\pi)\int_0^{2\pi} d\theta \int_0^\infty dt\, p_x \exp[-t/\tau(p)] , \quad \text{(A1)}$$

where the collision rate is $1/\tau \equiv 4\sigma p/mV$. The hard-disk diameter is σ, $2p/m$ is the relative velocity, and V is the (two-dimensional) "volume" of each two-particle system. The integration over time gives

$$\int_0^\infty I dt = (1/2\pi) p_0 \tau_0 \int_0^{2\pi} (p_x/p) d\theta \ , \qquad \text{(A2)}$$

where τ_0 is the before-field collision time $1/\tau_0 = 4\sigma p_0/mV$. The integral of this well-behaved integrand was evaluated by Gaussian quadrature. Sixteen points were sufficient.

The isothermal case (iii) involves the use of a thermostat. As in Ref. 3, the corresponding equation of motion, in polar momentum coordinates with $p = p_0 \times (\cos\theta, \sin\theta) = (p_x, p_y)$ is

$$(d/dt) \ln[\tan(\theta/2)] = -E/p_0 \ . \qquad \text{(A3)}$$

From (A3), the post-field momentum p can be expressed in terms of the initial momentum (again making it possible to integrate over θ with a uniform before-field weight) and the field strength

$$\tan(\theta/2) = \tan(\theta_0/2) \exp(-E\Delta t/p_0) \ . \qquad \text{(A4)}$$

In this case the collision rate does not change with increasing field. This is because the combined effect of the field and thermostat is simply to rotate the momentum vector without changing its magnitude. The current integral $\int (p_x/p) d\theta$ can again be evaluated with 16-point Gaussian integration.

In the limit of very high fields the mobilities for the adiabatic and isothermal cases coincide. In the adiabatic case the integrand (p_x/p) in (A2) approaches unity. Dividing the integral by field strength gives a dimensionless mobility which approaches zero as $p_0/E\Delta t$. In the isothermal case the current integral $\int I dt$ approaches $p_0\tau_0$ at high fields and again the dimensionless mobility approaches zero as $p_0/E\Delta t$.

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