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Nonlinear Conductivity and Entropy in the Two-Body Boltzmann Gas

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We find exact solutions of the two-particle Boltzmann equation for hard disks and hard spheres diffusing isothermally in an external field. The corresponding transport coefficient, one-particle current divided by field strength, decreases as the field increases. This nonlinear dependence of the current on the field and the corresponding nonlinear dependence of the distribution function on the current are compared to the predictions of "single-time" information theory. Our exact steady-state distribution function, from Boltzmann's equation, is quite different from the approximate information-theory analog. The approximate theory badly underestimates the nonlinear decrease of entropy with current. The exact two-particle solutions we find here should prove useful in testing and improving theories of steady-state and transient distribution functions far from equilibrium.

KEY WORDS: Boltzmann equation; information theory; nonlinear transport.

1. INTRODUCTION

The scope of nonequilibrium computer simulations of many-body systems has widened substantially during the past ten years. New developments in many-body mechanics have made it possible to describe dissipative nonequilibrium systems at constant energy or at constant temperature. This has been accomplished by incorporating "nonholonomic" (velocity-dependent) constraints into the equations of motion. These constraints keep the energy or temperature constant despite the irreversible heat generated by

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dissipative processes. By making it possible to study periodic homogeneous nonequilibrium systems, the steady-state methods avoid the excessive size dependence associated with physical boundaries.

The new constraint methods, applied to molecular dynamics, have led to the simulation of nonequilibrium steady states of both fluids and solids far from equilibrium. The nonlinear flux dependences of diffusion,[1] viscosity,[2,3] and heat conductivity[4-6] have all been studied for the standard test case, a Lennard-Jones fluid at the triple point. Recently, thermal conductivities for purely repulsive inverse-power potentials[7] have been used to refine and extend Rosenfeld's very promising corresponding-states approach[8,9] to the transport properties of dense fluids.

We show here that the study of small systems can be of significant aid in reaching a theoretical understanding of the new methods for treating dissipation, particularly in cases far from equilibrium, and of the results from corresponding computer simulations. For small systems the analytic work necessary to stimulate theoretical advances is actually possible. For instance, 20 years ago, analytic work showed that two hard disks exhibit a phase transition very like the melting transition found in larger computer-simulation systems and real laboratory systems.[10] This same two-disk system is closely related to the cell models and hard-sphere perturbation models used to describe both many-body systems and real materials. By now, melting is generally much better understood, for both small and large systems. This has come about largely as a consequence of analyzing the results of computer simulations from the perspective of simple analytic models.

Our understanding of nonequilibrium flows is at present much more primitive. For this reason the insight gained here by the study of small systems should prove particularly useful. Some results are already available. Two disks, or two spheres, exhibit both dilatancy (pressure increase) and shear thinning (viscosity decrease) at high strain rates.[11,12] These same effects, well known for real materials, have also been found in many-body simulations of dense fluids.

Two-body systems have a conceptual and computational advantage of simplicity over three-or-more-body systems. The two-body hard-disk system has a simple phase space. Only two spatial coordinates and one momentum are required to describe a two-disk system with fixed energy and center of mass. Even hard spheres require only three momenta to treat a two-body system. Because the corresponding phase space distributions can be analyzed in detail, such small systems are worthy of careful study. Such analyses will assist the development of a theoretical approach to the description of systems "far" from equilibrium, such as the two-body system studied here. Far from equilibrium, the transport coefficients themselves become dependent upon the fluxes, so that "linear" constant-coefficient transport theory breaks down.

The many-body equations of motion, describing the flow of a current of "colored" particles, driven by a field, were derived and applied to a dense Lennard-Jones fluid by Evans *et al.*[1] The two-body equations of motion we use here are related to these many-body equations, but have a simpler structure. In Section 2 we describe the two-body equations of motion for periodic isothermal systems of two oppositely "colored" disks, or spheres. As before,[1] we use the word "color," (with colors of ± 1) instead of "charge," to avoid any suggestion of Coulomb interactions between the disks or spheres.

In Section 3 we formulate and solve the corresponding two-particle Boltzmann equation. This equation describes, formally, the way in which the distribution of velocities is affected by the particles' diffusion. From the velocity distribution other average properties of the system can be calculated. For a fluid diffusing in a field, the interesting nonequilibrium properties are the current and the entropy.

In a many-body system, with more than two particles, the "collision term" in the Boltzmann equation is quadratic in the velocity distribution function. Again, the two-body case is considerably simpler than the many-body case. The two-body collision term is linear in the velocity distribution rather than quadratic. The complete two-body Boltzmann equation is linear too, and relatively easy to solve. Although the Boltzmann equation is linear in f, the equation is *inhomogeneous* in the field strength E. The resulting solution, $f(E)$, is the complete microscopic velocity distribution function, from which the nonequilibrium current and entropy can be calculated, by integration.

For disks, our linear-equation solution of the Boltzmann equation is an *approximate* description of a two-disk system because we ignore the relatively small effect of anisotropic scattering. For spheres, our solution gives an *exact* description of the corresponding hard-sphere system because the scattering of two hard spheres is isotropic in the center-of-mass coordinate frame appropriate to our two-body system.

In Section 3 the hard-disk and hard-sphere distribution functions from the Boltzmann equation are analyzed to obtain the *nonlinear* decrease of a "conductivity" (one-particle current divided by field strength) with increasing field strength together with the nonlinear decrease of the nonequilibrium entropy with increasing current.

No quantitative theory exists for systems far from equilibrium. It seems likely that a fruitful approach will follow the lead of Jaynes[13–15] and Zubarev[16] in extending Gibbs' successful treatment of equilibrium systems. This "information-theory" approach seems promising, due to its apparent simplicity, but has not yet been applied to many-body computer-simulation problems and thereby developed into a useful computational tool. Stimulating such applications requires quantitative calculations, like those presented here. In Section 4, we compare our calculated results with the predictions of the simplest theoretical nonequilibrium model, instantaneous, or "single-time," information theory.[13,14]

2. ISOTHERMAL CONDUCTIVITY IN A TWO-BODY SYSTEM

We explicitly consider a two-body system with fixed center of mass and periodic boundaries. For simplicity, we emphasize the hard-disk system, but we treat the hard-sphere analog in a similar way. In either case, an external field of strength E accelerates particle 1 (color $+1$) in the positive x direction. Particle 2 (color -1) is accelerated in the negative x direction by the field. Because the color "charge" is unity, E has units of force rather than force divided by charge. The Newtonian equations of motion describing this situation,

$$\begin{aligned} \dot{x} &= p_x/m, \qquad & \dot{y} &= p_y/m \\ \dot{p}_x &= F_x \pm E, \qquad & \dot{p}_y &= F_y \end{aligned} \tag{1}$$

do not conserve the internal energy. Instead, the two-body Newtonian system gradually heats up by extracting energy from the external field. For small fields, linear-response theory establishes that this heating is a second-order effect, quadratic in the field. It therefore has no effect on the linear conductivity (one-particle current divided by field strength). But its analysis is fundamental to any nonlinear theory of transport and to the development of steady-state simulations.

In order to study a steady conduction process, in which the system's state fluctuates around a nonequilibrium steady state, we must extract the irreversible heat. This can be done in a variety of ways.[17] The simplest of these to analyze gives a constant-energy velocity distribution. This constant-energy constraint can be imposed by a simple "*ad hoc* rescaling" of the momenta as the calculation proceeds.[18] In solving systems of first-order differential equations of motion, such as the set (1), it is convenient to incorporate this velocity rescaling directly into the equations of motion. This procedure has a respectable basis in Gauss' "principle of least constraint",[1] which leads to forces resembling frictional forces. These additional forces, $\delta\dot{p}$, can maintain a steady nonequilibrium state, either isoenergetic or isothermal:

$$\dot{p} - (F \pm E) \equiv \delta\dot{p} = -\zeta p \tag{2}$$

Gauss' friction coefficient ζ can be chosen to keep the energy fixed:

$$\zeta = \Sigma(\pm E p_x/m)/\Sigma(p^2/m) \tag{3E}$$

or the temperature (kinetic energy) fixed:

$$\zeta = \Sigma[(Fp \pm E p_x)/m]/\Sigma(p^2/m) \tag{3K}$$

We use the kinetic-theory definition of temperature. In terms of the velocities (constant in magnitude) of the two disks we define $2(mv^2/2) = kT$, where k is Boltzmann's constant.

For dilute gases, the two choices (3) for ζ coincide, except during collisions. For hard disks or spheres the collisions are instantaneous and make no contribution to the diffusive particle current. There are subtle differences between these two approaches for hard particles when collisional transfer is important—that is, in the high-density case of viscous or heat transport. We expect to discuss these collisional effects in the near future.[19]

Here we consider only two particles with no net center-of-mass momentum. Thus the momenta of the two particles lie at opposite points, $p_1 = p$ and $p_2 = -p$, on a momentum circle (disks) or sphere (spheres), with a radius chosen to reproduce the fixed kinetic energy, $mv^2 = (p_1^2 + p_2^2)/2m$, of the system. Between collisions the momenta change, due to the particles' interaction with the external field and with the constraint force (2).

The momenta can be described with the help of plane polar coordinates (two dimensions) or spherical polar coordinates (three dimensions). In either case the equation of motion which results from combining (2) and (3) is

$$d\theta/dt = \pm E \sin\theta/mv \tag{4}$$

(with a $-$sign for particle 1 and a $+$sign for particle 2). In (4) v is the (constant) speed of either particle. Thus the dynamics of the two-body problem can be reduced to advancing the particles along the curvilinear trajectories given by the integration of this equation of motion (4) between successive isoenergetic or isokinetic collisions.

Two-body molecular dynamics simulations, despite the simplicity of the velocity distribution, require long calculations to overcome statistical fluctuations. Here we consider the relatively inexpensive alternative of solving the Boltzmann equation for the two-body problem. The Boltzmann equation provides the average, rather than the instantaneous, velocity distribution, so that fluctuations do not occur. The solution represents the behavior of an ensemble of similar systems, rather than that of a single system.

In the following section we formulate and solve the Boltzmann equation for two diffusing hard disks or spheres in the external field E. The corresponding solution for transient or steady viscous flows follows easily from this example.

3. BOLTZMANN EQUATION

The Boltzmann equation is based on the assumptions that successive collisions are binary (automatically correct in our case) and uncorrelated. The correlation assumption holds provided that (a) the density is low enough and that (b) the field is weak enough. The density must be relatively low in order to avoid spatial correlations between successive collisions. That is, the mean free path must be considerably greater than the mean interparticle spacing. The correlation assumption would fail for strong fields. If the field were not sufficiently weak, then the streaming motion induced by it might act to prevent collisions, inducing a collisionless streaming motion parallel to the field. The field must therefore induce sufficiently small momentum changes during the time between successive collisions.

We expect that the Boltzmann equation *does* furnish a useful low-density, weak-field description of our two-body system. The full equation,

$$\partial f/\partial t + (p/m)\,\partial f/\partial r + \partial(f\dot{p})/\partial p = (df/dt)_{\text{coll}} \tag{5}$$

can be simplified for a homogeneous steady state, in which the first two terms vanish. The external field E and the momentum-dependent thermostat force $-\zeta p$ must both be included in the third term. [See Eq. (2).] The differential $\partial(f\dot{p})/\partial p$, rather than just $\dot{p}\,\partial f/\partial p$, appears in (5) because the equations of motion (1) + (2) are *not* Hamiltonian, so that the sum $\partial\dot{q}/\partial q + \partial\dot{p}/\partial p$ is nonzero. The analytic or numerical treatment of these terms, and the "collision integral" $(df/dt)_{\text{coll}}$ follows that sketched for the viscous flow case.[11]

The solution found here is somewhat simpler, but also more general than that given for the viscous flow problem because here we find the transient solution, as well as the steady state. The present treatment is easy to apply in the viscous flow case too. But here, because this extension would be repetitious, and not specially illuminating, we treat only diffusion.

For two hard disks of diameter σ, with relative speed $2v$, the low-density collision rate $1/\tau$ is $2v(2\sigma)/V$, where V is the total "volume" (area). For spheres, the cross section $4\pi\sigma^2$ replaces 2σ. Thus the "relaxation-time" collision term $(df/dt)_{\text{coll}}$ is $(f_0 - f)/\tau$. For spheres, this relaxation-time "approximation" is *exact* because two spheres, with velocities v and $-v$ and a random impact parameter, scatter isotropically to produce f_0. Because temperature and speed are constants of the equations of motion (1)+(2) the collision rate $1/\tau$ is also constant.

Consider first the steady state. When the equations of motion (1)+(2) are expressed in the polar coordinates of Section 2, the left-hand side of the Boltzmann equation turns out to be linear in the field strength E. We use the small parameter ε to indicate the product of the collision time τ and the external field strength E, divided by mv. That is, $\varepsilon = \tau E/mv$. In the polar momentum coordinates the time-independent, spatially homogeneous Boltzmann equation becomes

$$\varepsilon(d/d\theta)[f \sin^{D-1}\theta] = \sin^{D-2}\theta[f - f_0] \tag{6}$$

where D is the number of dimensions, two for disks, and three for spheres. For convenience, we choose the equilibrium distribution, f_0, equal to unity.

The steady-state Boltzmann equation (6) is exact for hard spheres—subject only to the assumption that successive collisions are uncorrelated. For hard disks the preponderance of head-on collisions relative to glancing collisions introduces a correlation in the "gain" term [the term containing f_0 on the right-hand side of (6)].

The innocent appearance of the steady-state differential equation for f (6) conceals rather well the nasty nature of its solutions. Successive even derivatives (zeroth, second,...) of the solutions become singular at $\varepsilon = 1/1$, 1/3, 1/5 (disks) and 1/2, 1/4, 1/6,... (spheres). Despite this analytic complexity a complete solution of the full time-dependent equation (5), suitable for numerical work, can be found. For disks, this has the form

$$f(\theta, t) = f_i(\hat{\theta})(\sin\hat{\theta}/\sin\theta)[(\tan\tfrac{1}{2}\hat{\theta}/\tan\tfrac{1}{2}\theta)]^{-1/\varepsilon}$$
$$+ (f_0/\varepsilon)\int_\theta^{\hat{\theta}} [(\tan\tfrac{1}{2}\beta)/(\tan\tfrac{1}{2}\theta)]^{-1/\varepsilon}(d\beta/\sin\theta) \tag{7A}$$

where $\hat{\theta}$ is defined by the relation

$$\exp(\varepsilon t/\tau) = \tan\tfrac{1}{2}\hat{\theta}/\tan\tfrac{1}{2}\theta \tag{7B}$$

For spheres, additional factors $(\sin\hat{\theta}/\sin\theta)$ and $(\sin\beta/\sin\theta)$ multiply the two terms in (7A). This solution can be obtained relatively easily by following and extending the "exponential relaxation" method used in Reif's textbook.[20] The method is conventionally used to find approximate solutions of the Boltzmann equation for many-body systems. But the many-body approximate relaxation method becomes exact in our case because our two-particle systems exhibit neither velocity persistence nor a dependence of the collision rate on velocity.

To apply Reif's method to solving the Boltzmann equation (5) we construct f by classifying particles on the basis of their most recent collision. The resulting f is composed of two terms, describing two types of particles: (1) particles which have not collided at all since the initial condition f_i was specified, and (2) particles which have collided one or more times since time zero. The particles of type (1), which have not collided, are propagated forward in time from their initial velocity, described by the angle $\hat{\theta}$, to the angle θ. Particles of type (2) which have most recently collided at an angle $\beta < \hat{\theta}$ (at some intermediate time between zero and t) and have streamed from that angle to the current value θ also contribute to f. The two types correspond precisely to the two terms in (7A). In both cases the probability for successful (unscattered) streaming falls off exponentially with time. In the steady state the first term in the general solution (7) vanishes and the upper limit on the second term becomes π. Both the transient and steady solutions can be readily checked by direct substitution into the Boltzmann equation.

For relatively small values of the field strength E iteration of (6), the steady-state version of (7), is useful. Repeated iteration leads to the following steady-state series in ε for f:

$$1 + \varepsilon c + \varepsilon^2(2c^2 - 1) + \varepsilon^3(6c^3 - 5c) + \varepsilon^4(24c^4 - 28c^2 + 5) + \cdots \tag{8D}$$

$$1 + 2\varepsilon c + \varepsilon^2(6c^2 - 2) + \varepsilon^3(24c^3 - 16c) + \varepsilon^4(120c^4 - 120c^2 + 16) + \cdots \tag{8S}$$

where c is $\cos\theta$ and ε is again the small parameter $\tau E/mv$. These partial series, (8D) for disks and (8S) for spheres, are consistent with the limiting steady-state values for $f(0)$ and $f(\pi)$ [derivable from the time-independent differential equation (6)]:

$$\begin{aligned} f(0) &= 1/[1 - (D-1)\,\varepsilon] \\ f(\pi) &= 1/[1 + (D-1)\,\varepsilon] \end{aligned} \tag{9}$$

Corresponding series describe the one-particle current, $I = \langle p_1 \rangle$ and the nonequilibrium part of the entropy $dS/Nk = -\langle \ln f \rangle$:

$$I/mv = (1/2)\,\varepsilon - (1/4)\,\varepsilon^3 + \cdots \tag{10D}$$

$$I/mv = (2/3)\,\varepsilon - (8/15)\,\varepsilon^3 + \cdots \tag{10S}$$

$$dS/Nk = -(1/4)\,\varepsilon^2 + (3/32)\,\varepsilon^4 + \cdots \tag{11D}$$

$$dS/Nk = -(2/3)\,\varepsilon^2 + (4/15)\,\varepsilon^4 + \cdots \tag{11S}$$

By choosing the equilibrium f_0 equal to unity we avoid an additional constant contribution to the entropy.

Numerical solutions can be used to extend these series. An effective route to numerical solutions for ε up to 0.5 (disks) or to 0.35 (spheres) is to iterate the steady-state differential equation (6), using the series (8) as initial guesses. For the higher values of ε it is more convenient to integrate directly the steady-state limiting form of the general time-dependent solution (7). Representative currents and entropies are listed in Table I.

In Eq. (8)–(11) we have omitted terms of fifth and higher order in the external field. In the following section we compare these truncated results with the corresponding approximate currents and entropies from single-time information theory.

4. INFORMATION THEORY

The disk and sphere systems considered here are of interest because they illustrate both transient and steady nonequilibrium states, far from equilibrium. The two-body steady states can be analyzed theoretically, at low density, and are also amenable to computer simulation, at any density.

But for many-body systems under such conditions useful theories have still to be developed. Jaynes correctly suggested, about 30 years ago,[13,14] that not only equilibrium, but also nonequilibrium, systems could be treated from the ensemble viewpoint. His approach to a nonequilibrium

Table I. One-Particle Current $I = mv\langle \cos\theta \rangle$ and Nonequilibrium Entropy $dS/Nk = -\langle \ln f \rangle$ for Two Hard Disks as a Function of Collision Time τ, Field Strength E, Particle Mass m, and Speed v

$\varepsilon = (\tau E/mv)$	$I/\varepsilon mv$	$-dS/Nk$
0.0	0.5000	0.00000
0.1	0.4975	0.00249
0.2	0.4907	0.00986
0.3	0.481	0.0219
0.4	0.468	0.0381
0.5	0.455	0.0583
0.6	0.441	0.0822
0.7	0.427	0.1094
0.75	0.420	0.1242

Table II. One-Particle Current $I = mv\langle\cos\theta\rangle$ and Nonequilibrium Entropy $dS/Nk = -\langle\ln f\rangle$ for Two Hard Spheres as a Function of Collision Time τ, Field Strength E, Particle Mass m, and Speed v

$\varepsilon = (\tau E/mv)$	$I/\varepsilon mv$	$-dS/Nk$
0.00	0.6667	0.000000
0.05	0.6653	0.001665
0.10	0.6615	0.00664
0.15	0.6554	0.01487
0.20	0.6474	0.02629
0.25	0.6379	0.04079
0.30	0.6273	0.0583
0.35	0.6160	0.0787
0.40	0.6041	0.1020

ensemble theory has come to be called "information theory." The references should be consulted for a careful analysis of the theory's content. We take the risk of oversimplification by giving a one-sentence summary:

> If all of the information necessary to describe a system at time t is used to constrain the phase-space distribution function $f(t)$, then a variational construction of the distribution function (equivalent to maximizing Gibbs' entropy, $-k\langle\ln f(t)\rangle$, where $f(t)$ is the N-particle distribution function and k is Boltzmann's constant) will accurately describe the system.

At equilibrium, this approach reproduces Gibbs' (time-independent) statistical ensembles. Away from equilibrium the same general approach can still be used. But, as emphasized by Zubarev,[16] specifying the local thermodynamic state, as well as the velocity and nonequilibrium fluxes (i.e., the "hydrodynamic state," including local flows of mass, momentum, and energy) is still not a sufficient description. We will call the limited version of information theory, based on the current hydrodynamic state, the "single-time" theory. The single-time theory is not necessarily correct outside the range of validity of linear transport theory.

Why is the single-time theory wrong? What additional information could be missing if all of the local variables have been specified? We also need the explicit statement that these fluxes are steady in the time (assuming that we wish to describe a steady state). This approach can be made systematic, first finding the maximum entropy distribution with a specified current $\langle I\rangle$; then improving the variational calculation by adding the requirement that $\langle dI/dt\rangle$ also vanish; then $\langle d^2I/dt^2\rangle$,.... These successive restrictions on the distribution function improve the accuracy with which it satisfies the steady-state equation (6). Adding derivatives of I gradually increases the accuracy of the solution by constraining more Fourier components in its expansion.

It is clear that in this case it is much simpler to give up the variational approach altogether and to solve the kinetic equation (6) directly. The variational information-theory approach to dynamical many-body problems appears to be computationally much more involved than the molecular dynamics simulations it is intended to supercede.

Here we can compare our currents and entropies for a simple system with the predictions of the single-time theory. Because the single-time theory is correct close to equilibrium, it is necessary to consider the nonlinear conductivity in this comparison.

For our two-particle system the N-particle distribution function is, at low density, the solution of the two-particle Boltzmann equation. If we seek the distribution function which maximizes $-\langle \ln f \rangle$ subject to a fixed kinetic energy mv^2, fixed total momentum $p_1 + p_2 = 0$, and fixed average one-particle current, $\langle I \rangle = (\frac{1}{2}) \Sigma(\pm mv \int f \cos\theta \, d\theta / \int f \, d\theta$, the Lagrange multiplier solution (apart from a multiplicative normalization factor) is

$$f = \exp(\alpha \cos\theta) \tag{12}$$

where the Lagrange parameter α has to be chosen to reproduce the desired current. It is interesting that both the entropy expression $-k\langle \ln f \rangle$ and the one-particle current $mv\langle \cos\theta \rangle$ reduce to the same quotient of Bessel functions. By expressing the entropy in terms of the current $\langle I \rangle$, we can compare the theoretical prediction (12) with the solution of the Boltzmann equation (6). The information-theory predictions, from (12), are

$$I/mv = \langle \cos\theta \rangle = (1/2)\,\alpha - (1/16)\,\alpha^3 + \cdots \tag{13D}$$

$$I/mv = (1/3)\,\alpha - (1/45)\,\alpha^3 + \cdots \tag{13S}$$

$$dS/Nk = -\langle \ln f \rangle = -(1/4)\,\alpha^2 + (3/64)\,\alpha^4 = -\hat{I}^2 - (1/4)\,\hat{I}^4 + \cdots \tag{14D}$$

$$dS/Nk = -(1/6)\,\alpha^2 + (1/60)\,\alpha^4 = -(3/2)\,\hat{I}^2 - (9/20)\,\hat{I}^4 + \cdots \tag{14S}$$

where $\hat{I}$ represents the dimensionless current, I/mv. As before, we omit terms of fifth and higher order in the field. The results (13) and (14) can be directly compared to the steady Boltzmann equation solutions (10) and (11). The exact series give

$$dS/Nk = -\hat{I}^2 - (5/4)\,\hat{I}^4 - \cdots \tag{15D}$$

$$dS/Nk = -(3/2)\,\hat{I}^2 - (81/20)\,\hat{I}^4 - \cdots \tag{15S}$$

A comparison of these exact results (15) with the information-theory predictions given in Eq. (14) shows that the nonlinear terms quartic in the field are underestimated by factors of 5 and 9, respectively, in two and three dimensions. Information theory provides a greater entropy than the exact result (15) at the expense of not maintaining a steady distribution.

This disparity reflects qualitative differences between the exact and approximate distributions at moderate fields. At fields sufficiently strong to reveal the influence of the nonlinear terms, the exact solution of the Boltzmann equation has a qualitatively different shape from the Lagrange-multiplier solution of single-time information theory. This is illustrated in Figure 1. In the figure we compare an exact solution of the Boltzmann equation for two hard disks with a solution of the functional form given by information theory. This comparison, and the series (15), strongly suggest that the single-time or instantaneous version of the theory is not useful far from equilibrium. A useful approximation can probably be based on the use of a single relaxation time, leading to a simple time-integrated version of information theory resembling our exact solution (7) (with the additional requirement that the distribution function be steady in time).

Over the past two decades, the nonlinear nonequilibrium distribution function has been repeatedly formulated in terms of time integrals of the dissipated energy. This approach has most recently been put on a more nearly rigorous basis by Evans and Morriss,[21] who took advantage of the

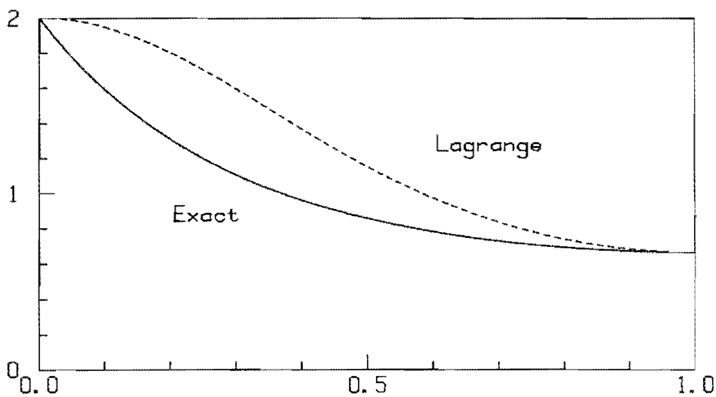

Fig. 1. Solution of the Boltzmann equation for two hard disks at $\varepsilon = \tau E/mv = 0.5$ (solid curve). The dashed curve is a single-time Lagrange-multiplier approximation from information theory. This latter distribution has been matched to the exact values of f at the end points $\theta = 0$ and $\theta = \pi$. The exact distribution function has an average value of unity. The abscissa is θ/π.

explicit form of the equations of motion preserving the energy, or the temperature, of dynamical systems. The result of their work is the same as Zubarev's.[16] It is unfortunate that all of these "theoretical" expressions for nonequilibrium steady states appear to be precisely equivalent to a prescription that the distributions are to be obtained by carrying out molecular dynamics simulations.

Exact solutions to nonlinear kinetic problems are rare. We expect that the exact solution (7) will be useful in formulating computationally effective forms of these nonequilibrium theories. As additional results become available for simple systems, such as the two hard particles treated here, more nearly operational nonequilibrium theories will be developed.

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