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ADIABATIC HAMILTONIAN DEFORMATION,

LINEAR RESPONSE THEORY, AND

NONEQUILIBRIUM MOLECULAR DYNAMICS

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I. INTRODUCTION

Systems far from equilibrium often involve shockwaves--regions only a few free paths in width with large gradients in density, velocity, and stress.[1] The research described here is _not_ directly concerned with shockwaves, but developed in a roundabout way from attempts to describe dense-fluid shockwaves[2] with Navier-Stokes continuum mechanics.[3] The Navier-Stokes approach to shockwave structure requires a complete knowledge of fluid properties in all of the thermodynamic states through which the material is driven by the shock process. In addition to the equation of state relating density, pressure, and energy, one must also know the state-dependent bulk and shear viscosities and the thermal conductivity. Because little was known about the state dependence of the bulk viscosity I set out to develop a computational method for measuring that viscosity in computer experiments incorporating adiabatic deformation.

The resulting computational scheme for bulk viscosity has led to a general Hamiltonian formulation for adiabatic deformations, useful for solids as well as fluids. A Hamiltonian formulation is desirable for any dynamical problem. It provides not only microscopic equations of motion, but also access to a well-developed time-dependent perturbation theory. Here I describe, in turn, the way the new Hamiltonian appeared, the consequences of applying linear-response perturbation theory to the Hamiltonian description of adiabatic deformation, and finally, the results of numerical calculations based on the corresponding Hamiltonian equations of motion.

The numerical calculations strongly suggest that dense-fluid transport coefficients exhibit frequency dependence large enough to detect in real laboratory experiments.

II. HAMILTONIAN DESCRIPTION OF ADIABATIC DEFORMATION

Consider a macroscopic continuum undergoing a homogeneous deformation described by a strain-rate tensor ∇u. If we choose for the origin a location where ∇u vanishes, then the local velocity $\dot{q}$ is $q \cdot \nabla u$. For illustrative purposes we chose a simple shear deformation, with the x displacement proportional to the y coordinate:

$$\dot{x} = \dot{\epsilon} y . \tag{1}$$

If this continuum deformation were suddenly applied, for a short time dt, to every particle in an atomistic many-body system, then the energy would change in a way dependent upon the initial particle coordinates. With a pairwise-additive potential energy, $\Phi = \sum \phi$, the (potential) energy change could be written in terms of the pair-force contributions to the pressure-tensor component P^{ϕ}_{xy} :

$$dE = d\Phi = \sum (d\phi/dr)(dr/dx)\Delta x = \sum \phi'(xy/r)\dot{\epsilon}dt = -P^{\phi}_{xy}V\epsilon . \tag{2}$$

Thermodynamics suggests, on the other hand, that in a <u>real</u> shear deformation the kinetic part of P_{xy} would also do work, causing a corresponding change in the kinetic energy K:

$$dK = - d\sum mv_x v_y = - P^k_{xy}V\epsilon . \tag{3}$$

If the Hamiltonian $H(q,p)$ describing the system included a term $\sum yp_x\dot{\epsilon}$, then the kinetic-energy change (3) would arise naturally. The Hamiltonian equations of motion ($\dot{q} = \partial H/\partial p; \dot{p} = -\partial H/\partial q$) would provide additional accelerations,

$$\Delta p_y = -\dot{\epsilon}p_x . \tag{4}$$

The resulting kinetic-energy change would agree with (3).

The need for momentum scaling, not just coordinate scaling, in adiabatic deformation, can most easily be appreciated in the ideal-gas case. Consider the homogeneous expansion of a monatomic ideal gas, with a linear strain rate $\dot{x}/x = \dot{y}/y = \dot{z}/z = \dot{\epsilon} = (1/3)\dot{V}/V$. In this case the inclusion of a term $\sum q \cdot p \dot{\epsilon}$ in the Hamiltonian would not only reproduce the macroscopic deformation, but would also provide accelerations, $\dot{p} = -\dot{\epsilon}p$, leading to adiabatic cooling. The resulting

rate of change of the kinetic energy with strain rate,

$$\dot{E} = \sum p \cdot \dot{p}/m = -(2/3)E(\dot{V}/V), \tag{5}$$

gives <u>exactly</u> the thermodynamic ideal-gas energy-volume relation for adiabatic expansion, leading to a pressure varying as the 5/3 power of the number density.

The two kinds of deformation just described, shear and dilatational, as well as longitudinal or mixed ones, can <u>all</u> be systematically and compactly described. Each corresponds to the addition of a perturbation to the usual equilibrium Hamiltonian,

$$H = H_{eq} + \sum qp:\nabla u ; \tag{6}$$

$$H_{eq} = \sum (p \cdot p/2m) + \sum \phi .$$

The perturbing term is the double-dot product of Doll's Tensor[4] $\sum qp$ and the strain rate tensor ∇u. The double-dot notation in (6) indicates that all nine terms of the form $\sum q_i p_j \nabla_i u_j$ are included in the product.

Adiabatic deformations could be carried out, in computer experiments, by interjecting occasional sudden coordinate and momentum scalings such as (1) and (4) into otherwise conventional solutions of Newton's equations of motion. It is preferable to incorporate deformation smoothly in the equations of motion, as suggested by the Hamiltonian (6). Then the equations of motion,

$$\dot{q} = (p/m) + q \cdot \nabla u ; \tag{7}$$

$$\dot{p} = F - \nabla u \cdot p ,$$

describe a continuous adiabatic process.

Just as in the equilibrium case, the equations of motion (7) derived from the Hamiltonian (6) are dynamically reversible, provided only that the macroscopic strain rate ∇u is reversed along with the particle velocities. The momenta from (6) have a simple interpretation—they are the product of mass with velocity in a frame moving with the local macroscopic velocity:

$$p \equiv m(\dot{q} - q \cdot \nabla u) . \tag{7a}$$

The equations of motion are also in exact agreement with the thermo-dynamic relation for an adiabatic deformation,

$$\dot{E} = \sum -F \cdot \dot{q} + \sum (p/m) \cdot \dot{p} \equiv -VP:\nabla u, \qquad (8)$$

where we use the microscopic global definition of the pressure tensor P:

$$PV \equiv \sum Fq + \sum (pp/m) . \qquad (9)$$

This pressure tensor is exactly the average momentum flux within the periodic volume V. It is not a surface interaction, measured across a system boundary, so that our global adiabatic deformation scheme does not apply accurately to deformations with very large pressure gradients, such as those found in strong shockwaves.

Hans C. Andersen[5] independently and simultaneously discovered a hydrostatic form of the Hamiltonian (6). His aim was to develop a formulation for constant-pressure molecular dynamics, fixing the mean pressure by allowing volume fluctuations. In our work the strain rate is prescribed and produces fluctuations in the pressure tensor. In either case the equations of motion can readily be solved numerically. The velocity must be adjusted whenever a particle crosses a moving periodic boundary. The momentum is unchanged in such a crossing, but the momentum is measured relative to a local velocity, and the local velocity is generally different on two opposite sides of the periodic volume V.

The Hamiltonian formulation just described for adiabatic mechanical work has no known analog describing isochoric heat flow. The micro-scopic analog of the thermodynamic relation dE = TdS has not been found. Despite considerable effort, this challenge remains.

III. LINEAR RESPONSE THEORY

For small strain rates the adiabatic deformation described by ∇u can be treated as a small perturbation to the Hamiltonian H_{eq}. Linear-response theory can then be used to calculate the resulting (viscous) nonequilibrium properties. Zwanzig's review[6] is the classical reference to the fundamental work of Green, Kubo, and Mori. A useful detailed account appears in McQuarrie's recent text.[7]

If we imagine that a shear perturbation $\sum qp:\nabla u$ is added to the Hamiltonian at time zero, then, at time t, the internal energy has changed by ΔE, and the N-particle distribution function, from linear response theory, reflects that change:

$$f(q,p,t)/f_{eq} = \exp(\Delta E/kT) \doteq 1 - (1/kT)\int_0^t \nabla u:PVds . \qquad (10)$$

The averages of dynamical phase functions, such as the energy and the pressure tensor, as well as the few-body distribution functions, can be obtained from (10).[8] As an example, consider the kinetic part of $P_{xy}V$:

$$\langle p_x p_y/m \rangle_{noneq} = -\dot{\epsilon}V^2(1/kT)\int_0^\infty \langle P_{xy}(o)P_{xy}^k(t)\rangle_{eq}dt . \qquad (11)$$

In the usual Green-Kubo autocorrelation expression for P_{xy} the integrand contains a kinetic term $P_{xy}^k(0)P_{xy}^k(t)$, a potential term $P_{xy}^\phi(0)P_{xy}^\phi(t)$, and a "cross-term" $[P_{xy}^k(0)P_{xy}^\phi(t) + P_{xy}^\phi(0)P_{xy}^k(t)]$. Here we find that the kinetic part of P_{xy} contains the kinetic term and half the cross term. Thus, just as in the approximate Enskog theory, the cross term makes equal contributions to the kinetic and potential parts of the momentum flux.

The analogous calculation for bulk viscosity is particularly interesting for an inverse nth power repulsive potential, $\phi = \epsilon(\sigma/r)^n$. In that case the contributions of the potential-energy and kinetic-energy fluctuations can be directly related to the corresponding fluctuations in the mean pressure:

$$\delta\phi = -\delta K; \quad V\delta P = (n/3)\delta\phi + (2/3)\delta K; \therefore \delta P^\phi/\delta P^k = -n/2. \qquad (12)$$

The exact result, valid at all times, that the potential part of the (constant-energy) pressure fluctuation is $-n/2$ times the kinetic part is a useful check of correlation functions. For instance, consider the inverse 12th power soft-sphere potential. Equation (12), valid at any time, shows that for the fluctuations giving bulk viscosity the ratio kinetic:cross:potential is $1:(-12):36$, so that the potential contribution dominates, even at the lowest density. The extension of the simple soft-sphere relations between the potential and kinetic pressure fluctuations to more general force laws remains a challenge.

IV. NUMERICAL CALCULATIONS

A series of calculations was carried out[9] for the inverse 12th power soft-sphere potential. In that work the hysteresis associated with cyclic compression and dilation (with ∇u varying sinusoidally in the time) was used to find the density dependence of the soft-sphere bulk viscosity. The results from that investigation were surprising. The bulk viscosities found were less than the predictions of Enskog's theory by as much as a factor of seven. Although the calculations could not be pursued at very low densities, the moderate-density results varied approximately as the 3/2 power of density. A posteriori, it is possible to "understand" the marked disagreement between the numerical viscosities and the Enskog predictions, based on the relative size of normal-stress and shear-stress fluctuations in inverse nth-power fluids. The results point out the need for a replacement theory; hopefully it will appear in time for Enskog's 1984 Centennial.

In the more realistic Lennard-Jones case[8] a series of calculations near the triple point produced frequency-dependent bulk viscosities reasonably close to those obtained by integrating the appropriate Green-Kubo integrands, as measured by Levesque and Pollock. There is considerable reproducible number dependence in the small-system long-time behavior of the Green-Kubo integrands, so that the actual large-system "long-time-tail" behavior of these functions is still in doubt. The agreement between the non-equilibrium frequency-dependent bulk viscosities and the Green-Kubo integrals could be noticeably improved by adding a reasonable long-time tail, varying as $t^{-3/2}$, to the Levesque-Pollock data. The corresponding low-frequency viscosity exhibits a strong variation with frequency, $\sim\omega^{1/2}$, large enough to be observed in careful laboratory measurements reaching frequencies of order 10^8 or 10^9 hertz. Evans has found a similar strong frequency-dependence in the Lennard-Jones shear viscosity near the triple point.

It remains a puzzle that the shockwave simulations which originally motivated this work do not seem to show analogous frequency or wavelength effects. Comparisons of shockwave profiles from molecular dynamics[2,3] with those from Navier-Stokes continuum mechanics indicate that the effective transport coefficients in strong shockwaves are not very different from those of ordinary long-wavelength low-frequency hydrodynamics. A theoretical understanding of the profile similarity is desirable.

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V. CONCLUSION

Although Hamiltonians of various kinds have previously been used to derive Green-Kubo relations for the transport coefficients[6], the particular choice described here is uniquely related to thermodynamics. This nonequilibrium Hamiltonian formulation of fluid flow provides pedagogically simple routes to nonequilibrium fluxes and distribution functions, to theoretical understanding of long-time effects, and to new numerical methods for simulating systems far from equilibrium.

The same methods are now being applied to solid-phase problems.[10] At the relatively high frequencies used in the viscous fluid calculations described here, solids typically behave elastically. Lower frequencies lead to the formation of dislocations and other defects, making it possible to study plastic flow.

A property of the nonequilibrium equations of motion which might be profitably explored is their effective irreversibility. Because only a few particles are necessary to generate irreversible behavior, simulations using adiabatic deformations of the kind described here could perhaps elucidate the instability in the equations of motion responsible for irreversibility.

VI. ACKNOWLEDGMENT

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