DISCUSSION

(Tuesday morning)

HOOVER. *Cohen* commented on the unusual forces in the formalism used by Hoover and inquired about their consequences on such problems as ergodicity and stability. *Hoover* states in response:

The thermodynamic functions are usually phase functions. The 'unusual' forces are designed to explore regions of phase space characteristic of particular values of these phase functions. These equations reduce to the field-free results in the large system limit with less sensitivity to the boundaries at finite N. In the mechanical sense most equations of motion are unstable that is, a small initial perturbation causes large divergences in the trajectories at later times. The thermodynamic properties show no long term drift and in this thermodynamic sense the equations are stable.

Several questions were asked on the technique of nonequilibrium molecular dynamics. *Langer*, for example, noted that the thermostat is a mechanism for removing energy which imposes infinitely long range forces. He wondered if thermostating could be justified for a nonlinear system. *Hoover* referred to the results reported by Evans (this volume) which showed that numerical values of nonlinear (shear-dependent) viscosities for a given system at a given state point are essentially independent of the constant temperature or constant energy algorithem [see also the comment by Hoover, Moran and Ladd]. Hoover also argued that the perturbation introduced by the thermostat vanishes as $N^{-1/2}$. *Fixman* asked why the nonequilibrium fluxes should not be driven from the surface of the unit cell. Hoover pointed out that the earlier method of Ashurst [ref. 22 of his paper] involved reservoirs which set up the nonequilibrium states.

Following the discussion of Monday morning, the question of material frame indifference or the Principle of Objectivity arose again (see comment by Hoover for Monday). *Curtiss* asked if the Burnett equations disagree with the Principle for high rotational frame velocities. *Hoover* replied that the Burnett equations predict radial and angular components of the heat flux. The result is quoted in Chapman and Cowling. The Enskog modification makes the coefficient about five times larger, in good agreement with molecular dynamics. *Hess* added that material objectivity is in disagreement with the Boltzmann equation because continuum mechanics does not include Coriolis forces.

Kestin commented on the large normal pressure differences obtained from

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S. Dahler, Phys.
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observed phenomena

Hess submitted
The Doll's tensor
A22 (1980) 1690)
The Hamiltonian
coordinate system

$$\mathcal{H} = H + \sum_i P_i$$

where p^i is the
denoted by Greek
Now v is chosen to
particle i, viz., v
origin according to

$$v_\mu(r^i) = v_\mu^0 + \cdots$$

leads to

$$\mathcal{H} = H + v_\mu^0 P_\mu$$

where $P_\mu = \Sigma_i p_\mu^i$ is
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$$\mathcal{H} = H + v_\mu^0 P_\nu$$

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...e computer simulations of a dense fluid and the connection with the laboratory ...periments of Reiner who also found large differences for gases. He pointed out ...e experimental procedure had been questioned by G. Taylor. *Hoover* noted ...at a discussion on this matter is reported in section III of M. Theodosopulu and ...S. Dahler, Phys. Fluids **15** (1972) 1755. Their conclusion was that it was by no ...eans clear that experimental difficulties were solely responsible for the ...bserved phenomena.

Hess submitted the following:

The Doll's tensor Hamiltonian introduced by Hoover et al. (Phys. Rev. ...22 (1980) 1690) to simulate plane Couette flow can be derived as follows. ...e Hamiltonian $\mathcal{H}$ in the rest frame is related to the Hamiltonian H in a ...ordinate system moving with the velocity v by

$$\mathcal{H} = H + \sum_i p_\mu^i v_\mu, \tag{1}$$

...ere p^i is the linear momentum of particle i, Cartesian components are ...noted by Greek subscripts, the summation convention is used for them. ...ow v is chosen to be the local flow velocity of a fluid at the position of the ...rticle i, viz., $v = v(r^i)$. Expansion of this field about a conveniently chosen ...igin according to

$$v_\mu(r^i) = v_\mu^0 + r_\nu^i(\nabla_\nu v_\mu) + \cdots \tag{2}$$

...ads to

$$\mathcal{H} = H + v_\mu^0 P_\mu + \nabla_\nu v_\mu \sum_i r_\nu^i p_\mu^i + \cdots, \tag{3}$$

...ere $P_\mu = \sum_i p_\mu^i$ is the total linear momentum. For $P_\mu = 0$ and a plane Couette ...ow field (3) reduces to the Hamiltonian used by Hoover et al. Insertion of ...e general decomposition of the gradient of the velocity into its irreducible ...rts into (3) yields

$$\mathcal{H} = H + v_\mu^0 P_\mu + \omega_\mu L_\mu + \gamma_{\mu\nu} Q_{\mu\nu} + \tfrac{1}{3}\nabla \cdot v Q, \tag{4}$$

...ere $\omega = \tfrac{1}{2}\text{rot } v$ is the vorticity of the flow field, $\gamma_{\mu\nu}$ is the symmetric ...aceless part of $\nabla_\mu v_\nu$, $L = \sum_i r^i \times p^i$ is the total angular momentum and the ...antities $Q_{\mu\nu}$, Q are defined by

$$Q_{\mu\nu} = \sum_i [\tfrac{1}{2}(r_\mu^i p_\nu^i + r_\nu^i p_\mu^i) - \tfrac{1}{3} r_\lambda^i p_\lambda^i \delta_{\mu\nu}], \quad Q = \sum_i r_\lambda^i p_\lambda^i. \tag{5}$$

...seems worth mentioning that the terms involving P and L in (4) "commute" ...th H in the Poisson-bracket sense whereas the other two terms do not ...mmute. In a plane Couette flow one has $\omega \neq 0$. Application of the Doll's

tensor approach to computer simulations of vorticity force flow fields ($\omega =$:
as realized in a four-roller flow (planar biaxial) or in a uniaxial elongation
flow are desirable.

Hoover submitted this reply:

At present there is no useful computer-experiment method for simula
irrotational steady shear. In a *homogeneous* periodic system the angle
momentum has no useful meaning. At present, rotation can only be avoided
paying the price of k-dependence, as did Gosling et al. [E.M. Gosling, I:
McDonald and K. Singer, Mol. Phys. **26** (1973) 1745] or ω-dependence, as v
did [Phys. Rev. **A22** (1980) 1690].

DESAI. *Editor's Note. Desai showed a movie of droplet formation i*
two-dimensional system. Kawasaki asked Desai about the physical origin of ::
$t^{1/2}$ *drop growth rate for his two-dimensional system. Desai submitted* ::
following:

To understand the cluster growth laws ($t^{1/2}$ for constant temperature sim
lation and $t^{1/3}$ for constant energy simulation) we have done asympto:
analysis analogous to that of Lifshitz and Slyozov for a binary mixture. 0:
system is a one component, two-dimensional fluid. From the trajecto:
snapshots and the movie that I showed, we note that at long times in a
constant-temperature simulation, the vapor atoms seemed to move kinet:
tically (not diffusively). Thus in our asymptotic analysis, we constructe:
rate equation for the number of atoms in a typical cluster in which the cur::
across the cluster surface is made up of gain and loss terms: the gain term:
obtained from the low density kinetic theory and contains time depende:
supersaturation (vapor density); the loss term is obtained from the class::
nucleation theory. The result is that asymptotically the cluster radius grows:
$t^{1/2}$. For the constant energy simulation on the other hand, the $t^{1/3}$ law can:
explained by modifying Lifshitz-Slyozov analysis to a one-component syste:

Hess added that the $t^{1/2}$ growth rate means that the area of a tv
dimensional cluster grows linearly with time: the area growth rate is de:
mined by the chemical potential. He then asked if the temperature depe
dence of the growth rate is in agreement with the chemical potential pred:
tion. *Desai* remarked that the temperature dependence has not yet be
studied.

Fixman referred to the movie of the system and asked why circu
droplets were not formed and if this could affect the coefficient of the grov:
rate. *Nelson* remarked that the roughness of the drops observed is chara
teristic of two-dimensions: small droplets will not be round.

ERPENBECK. Discussion centered on possible disagreements betwe
results reported from the various NEMD procedures. *Evans*, in particu

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questioned apparent discrepancies from some earlier work. *Erpenbeck*, however, communicated that the discrepancies now seem to be nonexistent within the statistical errors. *Evans* also remarked that the periodic boundary condition used with Doll's tensor methods were described incorrectly in Erpenbeck's paper. The Doll's tensor Hamiltonian is used in conjunction with Lees–Edwards boundaries. *Erpenbeck* replied that he was grateful to Evans for stressing this point.

Hoover (with B. Moran and A.J.C. Ladd, Dept. of Applied Science, University of California, Davis/Livermore) communicated the following comment on Erpenbeck's paper:

Erpenbeck's work stimulated us to compare adiabatic shear viscosities for soft spheres with those calculated isothermally by Evans and Hanley, and with those using Ashurst's reservoir technique (see table I). Evans' data at a reduced density of 0.70 and his fit at a reduced density of 0.75 are indicated by (E) and will appear in the Journal of Chemical Physics and Molecular Physics. Hanley's results at a reduced density of 0.80 are indicated by (H) and were sent us by him on 15 July 1982. Ashurst's calculations (A) appear in his 1974 Ph.D. thesis. The present adiabatic work is indicated by (P). If the pair potential is $\phi = \epsilon(\sigma/r)^{12}$, then the reduced viscosity depends only upon the reduced density and reduced strain rate

$$\eta\sigma^2[\epsilon/kT]^{2/3}[m\epsilon]^{-1/2}(N\sigma^3[\epsilon/kT]^{1/4}/\sqrt{2V}, \dot{\epsilon}\sigma[m/\epsilon]^{1/2}[\epsilon/kT]^{7/12}) = \eta^*(\rho^*, \dot{\epsilon}^*).$$

The data are shown in the stereo figure (fig. 1) and tabulated below. The present calculations all involve 64 particles in a cubic volume, with periodic boundaries. The total strain is expressed in terms of the shear strain per run,
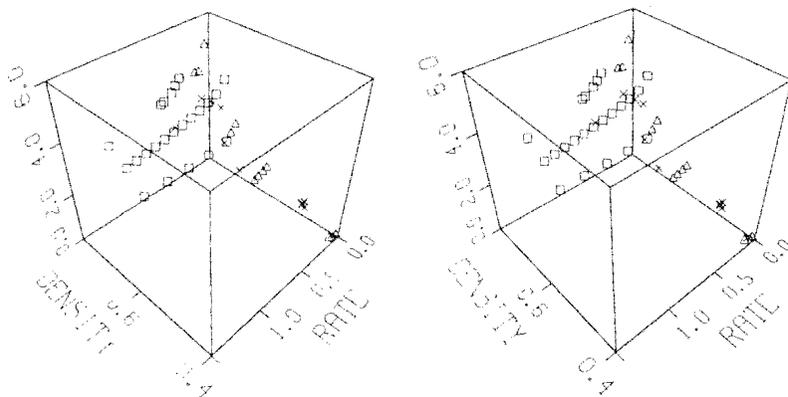
Fig. 1. Soft-sphere viscosities from Ashurst (triangles), Evans and Hanley (squares), and Hoover, Moran and Ladd (crosses).

DISCUSSION

TABLE I.
Soft sphere viscosity as a function of strain rate $du_x/dy = \dot{\epsilon}$

Density ρ^*	Strain rate $\dot{\epsilon}^*$	viscosity η^*	Method*	Source
0.687	0.215	2.17	$dT/dt = 0$	E
0.688	0.432	2.08	$dT/dt = 0$	E
0.690	0.652	2.02	$dT/dt = 0$	E
0.693	0.878	1.97	$dT/dt = 0$	E
0.696	1.109	1.91	$dT/dt = 0$	E
0.750		$\eta^* = 3.86 - 1.25\dot{\epsilon}^{*1/2}$	$dT/dt = 0$	E
0.800	0.349	4.18	$dT/dt = 0$	H
0.800	0.395	3.98	$dT/dt = 0$	H
0.800	0.440	3.81	$dT/dt = 0$	H
0.800	0.529	3.60	$dT/dt = 0$	H
0.800	0.560	3.55	$dT/dt = 0$	H
0.800	1.114	3.05	$dT/dt = 0$	H
0.400	0.05	0.33 ± 0.1	Rsvr	A
0.400	0.16	0.50 ± 0.1	Rsvr	A
0.600	0.05	1.44 ± 0.1	Rsvr	A
0.600	0.10	1.38 ± 0.04	Rsvr	A
0.600	0.16	1.30 ± 0.02	Rsvr	A
0.600	0.21	1.25 ± 0.04	Rsvr	A
0.700	0.05	2.54 ± 0.02	Rsvr	A
0.700	0.11	2.27 ± 0.06	Rsvr	A
0.800	0.05	5.00 ± 0.06	Rsvr	A
0.800	0.12	4.05 ± 0.13	Rsvr	A
0.800	0.17	4.14 ± 0.12	Rsvr	A
0.400	0.118	0.47 ± 0.01	10×25	P
0.481	0.091	0.79 ± 0.10	5×4	P
0.490	0.076	0.86 ± 0.16	2×8	P
0.491	0.038	0.81 ± 0.07	5×8	P
0.493	0.057	0.73 ± 0.10	3×9	P
0.631	0.273	1.52 ± 0.04	4×9	P
0.686	0.249	2.21 ± 0.09	3×8	P
0.735	0.098	3.02 ± 0.10	5×29	P
0.747	0.152	3.20 ± 0.07	3×36	P
0.765	0.535	2.84 ± 0.04	1×110	P
0.767	0.216	3.39 ± 0.04	2×190	P

* We indicate the total shear strain here for the present calculations.

$(\Delta x_{top} - \Delta x_{bottom})/L_y$, times the number of runs. The system heats somewhat during each run.

We conclude, from these results, that the difference between the shear viscosity found isothermally (with the velocity continuously rescaled) and that found adiabatically (where the velocity is only rescaled at the end of

run described in the negligibly small. One might to the rescaling frequen reservoir calculations, w the homogeneous calcu the nonuniform isobaric sinks.

...described in the table) is, with current computational uncertainties, negligibly small. One might well expect that the viscosity would be insensitive to the rescaling frequency, and this is true for soft spheres. The external reservoir calculations, with temperature gradients, disagree somewhat with the homogeneous calculations. We presume this discrepancy mainly reflects the nonuniform isobaric density profile present in a system with external heat sinks.

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