Viscosity of a simple fluid from its maximal Lyapunov exponents

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We compute the viscosity η of a fluid consisting of a large number of particles, $N=108$ and 864, as a function of shear rate γ from its maximum and minimum Lyapunov exponents. The calculation is based on an extension of Smale's pairing rule of Lyapunov exponents for Hamiltonian systems to non-Hamiltonian systems in contact with a heat bath. The numerical values of these maximal Lyapunov exponents as a function of γ are determined using nonequilibrium molecular dynamics (NEMD) computer simulations. The $\eta(\gamma)$ computed this way agree with those obtained directly from NEMD within the experimental error of 2% for the triple-point $N=108$ system. A $\gamma^{1/2}$ dependence of $\eta(\gamma)$ for large γ is found up to a Péclet number of 5.

I. INTRODUCTION

Lyapunov exponents of a number of dynamical systems have been determined numerically.[1] Most determinations have been of the largest Lyapunov exponent because it is the easiest to calculate numerically. Although for systems with a few degrees of freedom, all Lyapunov exponents can be determined, the numerical calculation of all of the exponents for systems with more than ~ 50 particles or 300 degrees of freedom, becomes prohibitively time consuming and expensive, even with modern supercomputers. Most Lyapunov exponents have been computed for Hamiltonian systems in thermal equilibrium and only a few studies of Lyapunov exponents for nonequilibrium systems have been reported.[2]

Lyapunov exponents are not only of interest for the understanding of phase-space properties of dynamical systems. Recently it has been shown[3,4] that for thermostatted nonequilibrium steady states, i.e., systems subject to a thermodynamic force and in contact with a heat reservoir, the macroscopic transport coefficients, such as those that occur in the Navier-Stokes equations of hydrodynamics, are related to the sum of all the Lyapunov exponents. Since this connection involves the sum of *all* Lyapunov exponents, its practical use would appear limited.

Recently however, one of us[5] (G.P.M.) determined all the equilibrium and nonequilibrium Lyapunov exponents as a function of an imposed shear rate γ. This was done for thermostatted systems of $N=2,4,8$ particles interacting through an upshifted Lennard-Jones potential truncated at its minimum, the Weeks-Chandler-Anderson (WCA) potential (for a definition, see Sec. III). Analysis of the simulation data indicated a rule that for *all* γ, the arithmetic means of *each* conjugate pair of Lyapunov exponents are equal. (Conjugate pairs of Lyapunov exponents are defined by ordering the exponents according to their size: the largest and the smallest exponents, the second largest and the second smallest, *et seq.*) Thus the sum of all Lyapunov exponents could be determined from the values of the maximum and minimum Lyapunov exponents alone and the shear viscosity η could be determined from the shear rate dependence of the two maximal Lyapunov exponents, $\lambda_{\max}$ and $\lambda_{\min}$, alone.

The calculation of negative Lyapunov exponents presents numerical difficulties. For most algorithms used to calculate Lyapunov exponents, the largest exponent is the easiest to determine followed by the second largest, the third largest, etc. Hoover *et al.*[2] calculate negative Lyapunov exponents by analyzing, in reversed time order, *stored* points, previously generated along a forward-time trajectory.[2] We adopt a more direct approach by calculating $\lambda_{\min}$ as the negative of the *maximum* Lyapunov exponent of a simulation that is *carried out* in negative time, by reversing the direction of the time. We calculate $\lambda_{\max}$ as the maximum Lyapunov exponent of a nonequilibrium steady state while $\lambda_{\min}$ is the negative of the maximum Lyapunov exponent of that steady state which evolves in negative time from the steady state used to calculate $\lambda_{\max}$.

By combining the conjugate pairing rule with this simple method of calculating the maximal Lyapunov exponents, the desired transport coefficient is easily calculated. This method of determining, for example, the shear viscosity may well be competitive with existing methods of direct evaluation from the Green-Kubo formula or with nonequilibrium molecular dynamics (NEMD).[6] Typical computation times on our Apollo DN 10000 for our preliminary calculations so far have been 10 h for low shear rates and 5 h for high shear rates.

In order to calculate the limiting zero shear rate Navier-Stokes viscosity $\eta(0)$, the same extrapolation to $\gamma=0^+$ is needed here as in NEMD.[6] Agreement between the Lyapunov and the direct NEMD methods to calculate $\eta(0)$ is within the experimental accuracy of about 6%. However, in common with NEMD and unlike the Green-Kubo method, the present algorithm succeeds in calculating the nonlinear shear rate dependent shear viscosity $\eta(\gamma)$. This allows us to verify the experimentally observed $\gamma^{1/2}$ dependence of $\eta(\gamma)$ (Refs. 6–8) up to very high shear rates.

II. OUTLINE OF PREVIOUS WORK

In order to place our results for Lyapunov exponents of dissipative systems in context, we briefly mention some previous work with no attempt to be complete. Lyapunov exponents for simple dynamical systems have been determined for many years now. Thus Livi, Politi, and Ruffo[9] numerically determined the complete Lyapunov exponents for the Fermi-Pasta-Ulam (FPU) β model for various numbers of oscillators, $N=40-80$. For $\beta=0.1$ and sufficiently large energy densities, $e=E/N>e_c\sim 0.35$, they found that a thermodynamic limit existed for the spectrum of the Lyapunov exponents, so that (keeping N/L constant, when L is the length of the system) the ith Lyapunov exponent for a system of N oscillators $\lambda(i,N)$ becomes independent of N for large N. For $N=160$ and 320, they determined a number of the largest Lyapunov exponents.

Since the FPU model is a Hamiltonian system the Lyapunov exponents exist in conjugate pairs with equal values but opposite signs, so that their sum also vanishes, i.e., $\sum_{i=1}^{N}\lambda(i)=0$.

A different many-body system consisting of a three-dimensional, $N=8$ particle system with a finite-range interparticle potential, $\phi(r)=\varepsilon[1-(r/\sigma)^2]^4$ where ε is the energy at interparticle distance $r=0$ and σ the cutoff length of the potential), was studied by Hoover and Posch.[3] Twenty-one equilibrium Lyapunov exponents were determined and a Debye-like Lyapunov spectrum was found. Away from equilibrium they studied diffusion by using an external field $\pm F_e$ to accelerate half the particles to the left and the other half to the right—the color field algorithm[6] for the self-diffusion coefficient. They noted that the sum of the Lyapunov exponents for such a system is negative and corresponds to the irreversible entropy production. As a consequence, a quadratic dependence of the nonequilibrium Lyapunov exponents on the external field was expected. Later Posch and Hoover[10] determined the full Lyapunov spectrum of $N=8,32$ particle, three-dimensional systems with a repulsive Lennard-Jones interaction. A nonequilibrium state was realized in the same way as before. The Lyapunov spectrum again exhibited a Debye-like power-law behavior. They also showed that the sum of all Lyapunov exponents indeed equals the rate of phase-space contraction as well as the irreversible entropy production for this model. In yet another paper[11] they studied the nonequilibrium Lyapunov spectra corresponding to planar Couette flow. They considered a system of N, two- or three-dimensional particles in a container with moving boundaries, so that a steady shear flow was induced. They determined all the Lyapunov exponents for systems up to $N=81$ particles in two dimensions and up to $N=27$ particles in three dimensions for reduced shear rates γ, $0<\gamma<2$. The shapes of the corresponding Lyapunov spectra were unlike those found earlier in three dimensions. They noted that the sum of conjugate pairs of Lyapunov exponents was negative instead of zero, consistent with their sum being negative and a contracting phase space. Using this, they obtained a relation between a viscosity coefficient $\eta(N,\gamma)$ and the *sum* of *all* Lyapunov exponents.

III. THE SYSTEM

In the present paper we study three-dimensional fluids of $N=108$ and 864 WCA particles,[12] that interact with a finite-range pair potential given by $\phi(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]+\varepsilon$ for $r<2^{1/6}\sigma$ and $\phi(r)=0$ for $r>2^{1/6}\sigma$. We consider these systems at a constant reduced energy per particle, $e=E/N\varepsilon=1.930\,10$ and at two reduced densities $n=n\sigma^3=0.4$ and 0.8442, where the latter is close to the triple-point density of a Lennard-Jones fluid.[12] The fluids are subject to a shear rate $\gamma=\partial u_x/\partial y$, i.e., a constant gradient of the x component of the local velocity u_x in the y direction. The particles of the fluid move according to the thermostatted SLLOD equations of motion,[6] i.e., the internal energy is kept constant by contact with an attached heat bath. The SLLOD equations of motion are then

$$\dot{\mathbf{q}}_i=\frac{\mathbf{p}_i}{m}+\mathbf{i}\gamma y_i\ , \tag{1a}$$

$$\dot{\mathbf{p}}_i=\mathbf{F}_i-\mathbf{i}\gamma p_{y_i}-\alpha\mathbf{p}_i\ . \tag{1b}$$

All quantities in (1) are reduced by the parameters ε and σ of the Lennard-Jones potential that corresponds to the WCA potential. Thus $\mathbf{q}_i$ stands for $\mathbf{q}_i/\sigma=(x_i,y_i,z_i)/\sigma$, $\mathbf{p}_i$ for $\mathbf{p}_i/(m\varepsilon)^{1/2}$ the force on particle i, $\mathbf{F}_i$ for $\mathbf{F}_i/(\varepsilon/\sigma)$, t for $t(\varepsilon/m\sigma^2)^{1/2}$, and γ for $\gamma(m\sigma^2/\varepsilon)^{1/2}$ [for argon $(\varepsilon/m\sigma^2)^{1/2}\approx 5\times 10^{11}$ Hz]. In all that follows we will use only dimensionless reduced quantities. $\mathbf{i}$ is a unit vector in the x direction. The $\mathbf{p}_i$ are peculiar momenta, defined in terms of the peculiar velocities, i.e., the velocities of the particles with respect to the (local) fluid velocity $u_x(y)=\gamma y$. The last term in (1b) removes heat, generated by the work done by the shear forces γ, from the system so as to keep the instantaneous internal energy, $H_0=\sum_i(p_i^2/2m)+\Phi(q)$, fixed. q stands for the set $\{\mathbf{q}_i\}$ $(i=1,\ldots,N)$. This can be accomplished by introducing, after Gauss,[13] a Lagrange multiplier α that takes the value[6]

$$\alpha=P_{xy}\gamma V\Big/\sum_i p_i^2\ , \tag{2}$$

where P_{xy} is the xy element of the instantaneous pressure tensor,[6]

$$P_{xy}V=\sum_i(p_{xi}p_{yi}/m+F_{xi}y_i)\ . \tag{3}$$

Equations (1) are equivalent to Newton's equations of motion in the presence of frictional forces $-\alpha\mathbf{p}_i$, if a con-

stant shear rate γ is imposed on the fluid at $t=0$.[6] The equations of motion (1) are supplemented by Lees-Edwards periodic boundary conditions.[6,14] In their adiabatic form, i.e., for $\alpha=0$, the SLLOD equations of motion give an exact description of adiabatic planar Couette flow arbitrarily far from equilibrium.[6] We note that the SLLOD equations of motion cannot be derived from a Hamiltonian.

The procedure we used to calculate the maximal Lyapunov exponents for the equations of motion (1) was the following. We used a trajectory obtained from Eqs. (1) at zero shear rate, i.e., for $\gamma=\alpha=0$, and for which Hamilton's (or Newton's) equations hold, to generate starting states in phase space for our nonequilibrium, i.e., $\gamma\neq 0$, $\alpha\neq 0$, calculations (cf. Fig. 1). The equations of motion were integrated using a fourth-order Runge-Kutta algorithm. The reduced time step used in this work was $\Delta t=0.004$. Every 100 time steps a group (group 2) of nonequilibrium trajectories was initiated from this zero shear rate trajectory. These nonequilibrium trajectories were followed for 1600 time steps using the SLLOD equations of motion (1). We assumed that from 1200 to 1600 time steps the nonequilibrium systems were sufficiently relaxed toward a nonequilibrium steady state (SS), that the SS maximal Lyapunov exponents could be determined. This was checked by computing SS ensemble averages for the shear stress and the hydrostatic pressure and ascertaining that they were essentially time independent for $t>1200\Delta t=4.8$. The SS maximum Lyapunov exponent was calculated by considering the growth in distance between two nearby trajectories.

Thus at the 1200th time step a new group (group 3), of trajectories was begun. These trajectories employed exactly the same equations of motion as the second group of trajectories. The strain rate was the same and the trajectories were run at constant internal energy. The initial phase for the third group, $\Gamma(3,0)$, was obtained by very slightly displacing the phases at the 1200th time step, $\Gamma(2,1200\Delta t)$, from the second group. The initial displacement distance, $d(0)=\{[\Gamma(2,1200\Delta t)-\Gamma(3,0)]^2\}^{1/2}$ was set at 10^{-8}. The subsequent exponential growth of this distance, $\langle d(t)\rangle=\langle\{[\Gamma(2,t+1200\Delta t)-\Gamma(3,t)]^2\}^{1/2}\rangle=d(0)\exp(\lambda_{SS}t)$, enabled us to calculate the largest Lyapunov coefficient for the steady state, $\lambda_{SS}=\lambda_{max}$.

At a time $t=1600\Delta t=6.4$, the group-2 phases, $\Gamma(2,1600\Delta t)$, were used as the starting phase for yet another group (group 4), of trajectories. These trajectories evolved from $\Gamma(2,1600\Delta t)$, in *negative time* at the same strain rate magnitude and internal energy as group 2. (Note that since the strain rate is an odd function of time, it actually changes sign under time reversal.) The last group of trajectories (group 5) was obtained by applying small phase-space displacements to $\Gamma(2,1600\Delta t)=\Gamma(4,0)$ in the same way as group-3 trajectories were obtained from $\Gamma(2,1200\Delta t)$.

The group-4 and -5 trajectories evolve backwards in time in the steady state. A diagrammatic representation of the interrelations between the five groups of trajectories is given in Fig. 1. The maximum and minimum Lyapunov exponents were determined by averaging over the members of the groups, where typically each group consisted of ~ 200 members.

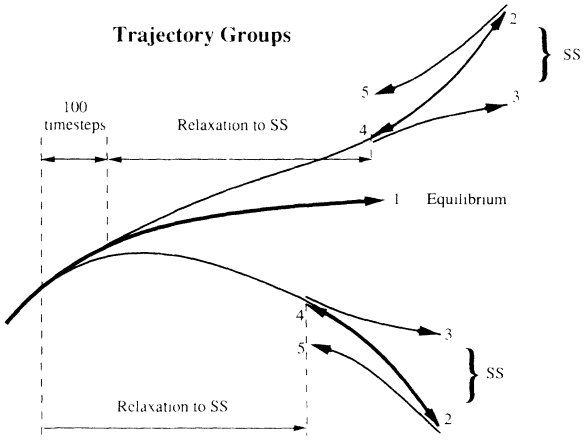

FIG. 1. We give a schematic representation of the generation of the various groups of trajectories. Group 1 is an equilibrium trajectory; group 2 is generated from group 1 by applying a shear; group 3 is generated from 2 after it has relaxed to the steady state (SS), by applying a slight phase-space displacement; group 4 originates from 2 after a time reversal and group 5 is generated from 2 by simultaneously applying time reversal and a slight phase-space displacement.

IV. LYAPUNOV SUM RULE FOR THE VISCOSITY

For the non-Hamiltonian dissipative system of Eqs. (1), the Liouville equation for the probability distribution function f in $6N$-dimensional Γ space reads[6]

$$\frac{df(\Gamma,t)}{dt}=-f\frac{d}{d\Gamma}\cdot\dot{\Gamma}=3N\alpha f\ . \tag{4}$$

Here d/dt is the material time derivative, $\Gamma=(q_{1x},p_{ix},\ldots,q_{Nz},p_{Nz})$, and a term of order 1 has been neglected.

On the other hand, if a small volume $V(\Gamma,t)$ contains a fixed number M of ensemble members and $f(\Gamma,t)=M/V(\Gamma,t)$, we find from the definition of the Lyapunov exponents λ_i that for ergodic systems

$$\int d\Gamma\frac{df(\Gamma,t)}{dt}=-\left\langle\frac{d\ln V(\Gamma(t))}{dt}\right\rangle=-\sum_{i=1}^{6N}\lambda_i\ , \tag{5}$$

where $\langle\ \rangle$ denotes a phase-space average. Combining (4) and (5), we obtain a relation between α and the sum of all Lyapunov exponents:

$$\langle 3N\alpha\rangle=-\sum_{i=1}^{6N}\lambda_i\ . \tag{6}$$

Our thermostat coupling constant α ensures that the rate of energy produced in the system in the stationary state, due to the work done on the system by the shear forces, is exactly balanced by the energy (heat) removed by the thermostat, so that

$$\dot{H}_0=-P_{xy}V\gamma-2K\alpha=-P_{xy}V\gamma-3Nk_BT\alpha=0\ . \tag{7}$$

K is the microscopic expressions for the instantaneous peculiar kinetic energy

$$K=\sum_i p_i^2/2m=3Nk_BT/2 \tag{8}$$

with k_B Boltzmann's constant and V the volume of the system. In the stationary state $\langle T(\Gamma)\rangle$ is the kinetic temperature of the nonequilibrium steady state.

Using that $dH_0/dt\equiv 0$ and that a viscosity coefficient $\eta(N,\gamma)$ can be defined from the steady state average $\langle P_{xy}\rangle=-\eta(\gamma)\gamma$, one has, from Eqs. (6) and (7),

$$\eta(N,\gamma)=\frac{-k_BT_{SS}}{V\gamma^2}\sum_{i=1}^{6N}\lambda_i(N,\gamma)\ , \tag{9}$$

where the N dependence of η and the λ_i are explicitly indicated. Equation (9) allows a determination of $\eta(N,\gamma)$ in terms of all the (nonequilibrium) Lyapunov exponents of the fluid, as has been done by Posch and Hoover[11] and Morriss.[5] We call Eq. (9) the Lyapunov sum rule for shear viscosity. The shear viscosity occurring in the Navier-Stokes equations is given by

$$\eta=\lim_{\gamma\to 0^+}\lim_{N\to\infty}\eta(N,\gamma)\ .$$

As mentioned before, the actual determination of η from (9) is hampered by the very large number of exponents in a macroscopic system. The arithmetic mean rule enables one to calculate the viscosity using (9) by eliminating the need to know all $6N$ Lyapunov exponents. Using this rule, Eq. (9) becomes

$$\eta(N,\gamma)=\frac{-3nk_BT_{SS}}{\gamma^2}[\lambda_{max}(N,\gamma)+\lambda_{min}(N,\gamma)]\ , \tag{10}$$

where $n=N/V$ is the number density of the system.

For a sufficiently large system, the N dependences of η and λ will disappear, so that then

$$\eta(\gamma)=\frac{-3nk_BT_{SS}}{\gamma^2}[\lambda_{max}(\gamma)+\lambda_{min}(\gamma)] \tag{11}$$

holds for the shear rate dependent viscosity.

V. CONJUGATE PAIRING OF CHARACTERISTIC EXPONENTS FOR THERMOSTATTED SHEARING SYSTEMS

Before we consider an outline of the proof of the conjugate pairing rule for thermostatted shearing systems described by the equations of motion given in (1a) and (1b) we will discuss conjugate pairing firstly for Hamiltonian systems and secondly for thermostatted Hamiltonian systems. The Hamiltonian case is well known[15] but the extension to thermostatted Hamiltonian systems which enables one to discuss the properties of dissipative nonequilibrium steady states, including shearing systems (1), is new.

Consider the equation of motion for a set of orthogonal tangent vectors, $\delta\Gamma_i(t)$, describing the progressive separation of two phase trajectories initially separated by $\delta\Gamma_i(0)$. The set $\{\delta\Gamma_i(t)\}$ forms a complete orthogonal basis for the tangent space with $\delta\Gamma_1(t)$ being parallel to the direction of fastest phase separation, $\delta\Gamma_2(t)$ being orthogonal to $\delta\Gamma_1(t)$ and $\delta\Gamma_1(t)\times\delta\Gamma_2(t)$ generating the fastest growing area, etc.[15] The equations of motion for the infinitesimal tangent vectors are

$$\frac{d}{dt}\delta\Gamma(t)\equiv\underline{T}(\Gamma)\cdot\delta\Gamma(t)=\frac{\partial\dot{\Gamma}(\Gamma(t))}{\partial\Gamma}\cdot\delta\Gamma(t) \qquad (i=1,\ldots,6N)\ . \tag{12}$$

The matrix $\underline{T}(\Gamma)$ is often called the stability matrix. It is a local matrix, depending on the phase point Γ. In the infinitesimal limit $\delta\Gamma(0)\to 0$ the formal solution of this equation can be written as[16]

$$\delta\Gamma(t)\equiv\exp_L\left[\int_0^t ds\ \underline{T}(\Gamma(s))\right]\cdot\delta\Gamma(0) \equiv\underline{L}(t)\cdot\delta\Gamma(0)\ , \tag{13}$$

where $\exp_L$ indicates a time-ordered exponential with the latest times s to the left. We will also need to refer to the Hermitian adjoint of Eq. (12), namely,

$$\frac{d}{dt}\delta\Gamma^\dagger(t)\equiv\delta\Gamma^\dagger(t)\cdot\underline{T}^\dagger(\Gamma)\ , \tag{14}$$

with solution

$$\delta\Gamma^\dagger(t)\equiv\delta\Gamma^\dagger(0)\cdot\exp_R\left[\int_0^t ds\ \underline{T}^\dagger(\Gamma(s))\right] \equiv\delta\Gamma^\dagger(0)\cdot\underline{L}^\dagger(t)\ , \tag{15}$$

where $\exp_R$ indicates a right-ordered exponential. For convenience we will now introduce two matrices $\underline{J}$ and $\underline{K}$ as

$$\underline{J}\equiv\begin{bmatrix}\underline{0} & \underline{I}\\ -\underline{I} & \underline{0}\end{bmatrix},\quad \underline{K}\equiv\begin{bmatrix}-\underline{I} & \underline{0}\\ \underline{0} & \underline{I}\end{bmatrix}\ , \tag{16}$$

where $\underline{I}$ is the $3N\times 3N$ identity matrix and $\underline{0}$ is the $3N\times 3N$ null matrix. For Hamiltonian systems, $\underline{T}$ satisfies the infinitesimally symplectic condition,[17]

$$\underline{T}^T\cdot\underline{J}=-\underline{J}\cdot\underline{T}\ . \tag{17}$$

It is known that this condition is satisfied if the matrix $\underline{T}$ can be written in the form

$$\underline{T}=\begin{bmatrix}\underline{A} & \underline{B}\\ \underline{C} & -\underline{A}^T\end{bmatrix}\ , \tag{18}$$

where the matrices $\underline{B}$ and $\underline{C}$ are symmetric and the superscript T indicates a transposed matrix.

It is easy to show that if $\underline{T}$ is real and satisfies the infinitesimally symplectic condition (17), then $\underline{L}$ satisfies the globally symplectic condition[17]

$$\underline{L}^T\underline{J}\,\underline{L}=\underline{J}\ . \tag{19}$$

The proof relies on the fact that

$$\exp_R\left[\int_0^t[-\underline{T}(s)]ds\right]\cdot\exp_L\left[\int_0^t\underline{T}(s)ds\right] =\exp_L\left[\int_0^t\underline{T}(s)ds\right]\cdot\exp_R\left[\int_0^t[-\underline{T}(s)]ds\right]=\underline{I}\ ,$$

the identity operator. It is also easy to show that if $\underline{T}$ is

infinitesimally symplectic then $\underline{L}^{T}\cdot\underline{L}$ is also globally symplectic.

The property of symplectic matrices we use here is that if $\underline{T}$ is infinitesimally symplectic with eigenvalue λ, then $-\lambda$ is also an eigenvalue. Furthermore if $\underline{L}$ (or $\underline{L}^{T}\cdot\underline{L}$) is globally symplectic and has an eigenvalue λ, then $1/\lambda$ is also an eigenvalue of $\underline{L}$ (or $\underline{L}^{T}\cdot\underline{L}$). Thus the eigenvalues of $\underline{L}^{T}\cdot\underline{L}$ are real and occur in conjugate pairs, $\lambda, 1/\lambda$. Now the Lyapunov exponents can be defined as the logarithms of the eigenvalues of the symmetric matrix $\underline{\Lambda}$,[15]

$$\underline{\Lambda}=\lim_{t\to\infty}\underline{\Lambda}(t)=\lim_{t\to\infty}[\underline{L}^{T}(t)\cdot\underline{L}(t)]^{1/2t} . \tag{20}$$

Equation (20) guarantees that the Lyapunov exponents occur in conjugate (Smale[18]) pairs, $\lambda_i,\lambda_{i'}$ $(=-\lambda_i)$. Since the stability matrix for all Hamiltonian systems satisfies the infinitesimally symplectic condition, (17), Smale pairing is observed for all Hamiltonian systems.

We will now discuss thermostatted Hamiltonian systems. In the theory of nonequilibrium steady states it is usual to employ peculiar momenta $\mathbf{p}_i$ (i.e., momenta relative to the local velocity of the fluid[6]). Thus the application of a Gaussian thermostat to a (symplectic) Hamiltonian system adds the usual $-\alpha\mathbf{p}_i$ thermostatting term to the momentum equation of motion as in (1b), and the stability matrix takes the form

$$\underline{T}\equiv\underline{T}'-\alpha\underline{I}/2\equiv\underline{T}^{\,\mathrm{ad}}-\alpha\underline{K}/2-\alpha\underline{I}/2 , \tag{21}$$

where we have dropped the Γ dependence of $\underline{T}$ and a term of $O(1/N)$ and all matrices are $6N\times 6N$. The addition of the thermostatting terms means that the stability matrix $\underline{T}$ no longer satisfies the infinitesimally symplectic condition (17). The matrix $\underline{T}^{\,\mathrm{ad}}$ is just the unthermostatted form of the stability matrix $\underline{T}$, obtained by setting $\alpha=0$. It is trivial to show that since for Hamiltonian systems $\underline{T}^{\,\mathrm{ad}}$ satisfies the infinitesimal symplectic condition (17), so does $\underline{T}^{\,\mathrm{ad}}-\alpha\underline{K}/2$. Thus the Lyapunov exponents of a system with local stability matrix $\underline{T}'\equiv\underline{T}^{\,\mathrm{ad}}-\alpha\underline{K}/2$ also occur in Smale pairs. The Lyapunov exponents for a thermostatted Hamiltonian system can be obtained from the eigenvalues of $\underline{\Lambda}(t;\alpha)$,

$$\begin{aligned}\underline{\Lambda}(t;\alpha)&=\left\{\exp_R\left[\int_0^t ds\left[\underline{T}'^{T}(s)-\frac{\alpha(s)}{2}\right]\underline{I}\right]\cdot\exp_L\left[\int_0^t ds\left[\underline{T}'(s)-\frac{\alpha(s)}{2}\right]\underline{I}\right]\right\}^{1/2t}\\&=\underline{\Lambda}'(t)\exp\left[-\int_0^t ds\,\alpha(s)\underline{I}\right]^{1/2t}\\&=\underline{\Lambda}'(t)\exp\left[-\frac{\langle\alpha\rangle}{2}\right]\underline{I}\end{aligned} \tag{22}$$

where $\langle\ \rangle$ denotes the obvious time average, or for an ergodic system, a phase-space average over the steady state. In deriving (22) we use that for all s,s', $\alpha(s)\underline{I}/2$ commutes with $\underline{T}'(s')$. The Lyapunov exponents λ_i of the thermostatted Hamiltonian system are the solutions of the determinantal equation,

$$|\underline{\Lambda}-\exp(\lambda_i\underline{I})|=\left|\underline{\Lambda}'\exp\left[-\frac{\langle\alpha\rangle}{2}\underline{I}\right]-\exp(\lambda_i\underline{I})\right|=0 . \tag{23}$$

From (23) it follows that

$$\left|\left[\underline{\Lambda}'\exp\left[-\frac{\langle\alpha\rangle}{2}\underline{I}\right]-\exp(\lambda_i\underline{I})\right]\cdot\left[\exp\left[\frac{\langle\alpha\rangle}{2}\underline{I}\right]\right]\right|=0 \tag{24}$$

so that

$$\left|\underline{\Lambda}'-\exp\left[\lambda_i+\frac{\langle\alpha\rangle}{2}\right]\underline{I}\right|=0 . \tag{25}$$

Since the eigenvalues of $\underline{\Lambda}'$ occur in conjugate pairs $\{\mu_i,\mu_{i'}(=1/\mu_i)\}=\{\exp(\lambda_i+\langle\alpha\rangle/2),\ \exp(\lambda_{i'}+\langle\alpha\rangle/2)\}$, the Lyapunov exponents will occur in conjugate pairs $\{\lambda_i+\langle\alpha\rangle/2,\lambda_{i'}+\langle\alpha\rangle/2\}=\{\ln(\mu_i)\ln(\mu_{i'}),[=-\ln(\mu_i)]\}$. This implies that conjugate pairs of Lyapunov exponents $\lambda_i,\lambda_{i'}$, for Gaussian thermostatted Hamiltonian systems obey the conjugate pairing rule

$$\lambda_i+\lambda_{i'}=-\langle\alpha\rangle=2\bar{\lambda} . \tag{26}$$

Here $\bar{\lambda}$ is the Lyapunov exponent that vanishes when $\gamma=\alpha=0$, and the dependence of the λ_i on γ has been suppressed. The sum of conjugate exponents, (26), is thus independent of the pair index i and is equal to the average Lagrange multiplier $-\langle\alpha\rangle$.

For SLLOD dynamics (1), the adiabatic stability matrix that corresponds to the stability matrix, $\underline{T}^{\,\mathrm{ad}}$, for Hamiltonian systems discussed above, does *not* satisfy the infinitesimal symplectic condition (17). However, one can easily prove that for $t>0^{+}$, SLLOD dynamics is identical to Newtonian or Hamiltonian dynamics.[6] This can be seen by eliminating the momenta from the adiabatic form of (1a) and (1b) yielding

$$\ddot{\mathbf{q}}_i=\frac{\mathbf{F}_i}{m}+i\gamma\delta(t)y_i , \tag{27}$$

where we assume that the shear rate takes the form of a Heaviside step function about $t=0$. (For a full discussion of SLLOD dynamics, the reader is referred to Ref. 6.)

Now for Newtonian mechanics the phase space is described in terms of the laboratory coordinates and momenta, $\{\mathbf{q}_i, m d\mathbf{q}_i/dt; i=1,\ldots,N\}$, while for SLLOD dynamics the phase space is described in terms of laboratory positions and peculiar momenta,

$$\{\mathbf{q}_i, \mathbf{p}_i \equiv m d\mathbf{q}_i/dt - i\gamma y_i; i=1,N\} .$$

This linear transformation of the phase-space coordinates leaves the eigenvalues of the local and global stability matrices unchanged. This is easily seen by applying this coordinate transformation to the respective eigenvalue equations. Alternatively one can see this by explicit comparison of the corresponding characteristic equations for the Newtonian and adiabatic SLLOD stability matrices. It is easy to show then that the eigenvalues of the adiabatic SLLOD stability matrix have *no* dependence on the shear rate.

The subsequent inclusion of a thermostat then proceeds as in the Hamiltonian case. We also note that the use of Lees-Edwards shearing periodic boundary conditions[6,14] does not change the fact that the matrix $\underline{C}$ in (18) is symmetric.

Thus although there is no Hamiltonian which can generate the adiabatic SLLOD equations of motion for shear flow, a modified pairing of Lyapunov exponents still occurs. Furthermore the Lyapunov exponents for thermostatted SLLOD dynamics, (1), obey the same conjugate pairing rule as their thermostatted Hamiltonian counterparts, namely, Eq. (26).

VI. RESULTS

In Fig. 2 we plot $\delta\lambda_i(\gamma) \equiv \lambda_i(\gamma) - \bar{\lambda}(\gamma)$, with $\bar{\lambda}(\gamma)$ defined in (26), for a three-dimensional $N=8$ particle shear flow, with periodic Lees-Edwards boundary conditions. We see that within estimated numerical uncertainties the data are in agreement with the conjugate pairing rule, Eq. (26). In Fig. 3 we plot the shift of the values of the Lyapunov exponents relative to those at equilibrium. We might expect that since the exponents measure the stability of phase-space trajectories, the shifts, $\Delta(i\gamma) \equiv \lambda_i(\gamma) - \lambda_i(0)$, would be a monotonically decreasing function of the exponent index i. This is indeed observed. In fact we see from Fig. 3 that the shifts seem to be a linear function of the exponent index, which is sufficient for the global form of Eq. (17) to hold, but not necessary.

In Fig. 4 we show a comparison of the viscosity computed directly from NEMD for $N=108$ WCA particles with the viscosity η_L computed from the Lyapunov exponents using Eq. (11). The system has a density that corresponds to a moderately dense gas. As can be seen

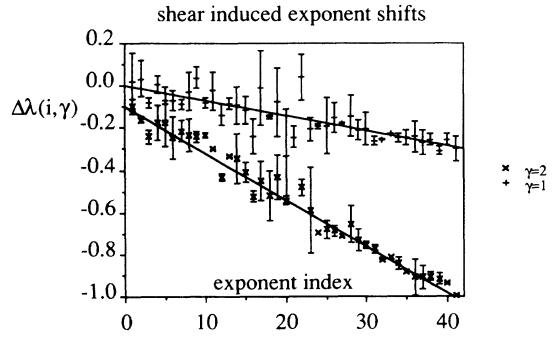

FIG. 3. For the same system as considered in Fig. 2, we show the shear induced shifts relative to equilibrium, $\Delta(i,\gamma) = \lambda_i(\gamma) - \lambda_i(0)$, in the Lyapunov experiments. The largest indexed exponents show the largest shifts. The shifts are apparently linear in the exponent index and asymptotically quadratic in the strain rate.

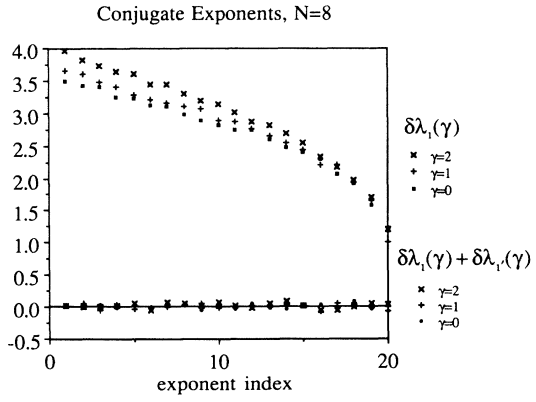

FIG. 2. The top three curves show $\delta\lambda_i(\gamma) \equiv \lambda_i(\gamma) - \bar{\lambda}(\gamma)$, $i < 6N/2$, for a three-dimensional system of 8 WCA particles in three dimensions. The state point considered is $T=1.0$, $n=0.4$. The lower three curves show $\delta\lambda_i(\gamma) + \delta\lambda_{i'}(\gamma)$. Our conjugate pairing rule, Eq. (26), predicts $\delta\lambda_i(\gamma) + \delta\lambda_{i'}(\gamma) = 0$, for all i,γ. This is clearly consistent with the data. The first exponent index corresponds to the largest Lyapunov exponent, exponent index 2 gives the second largest Lyapunov exponent, etc.

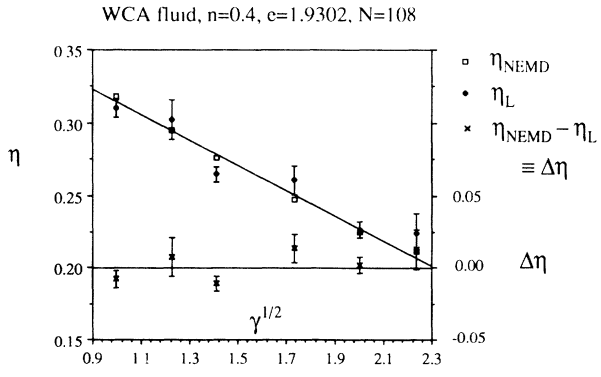

FIG. 4. Using Eq. (11) we compute the shear viscosity η_L for a system of 108 WCA particles directly from the Lyapunov exponents. This is compared with the standard NEMD calculation of the viscosity, η_{NEMD}, for the same system. The state points considered are $e=1.9302$ and $n=0.4$. Both sets of data are in agreement and are consistent with a linear dependence on $\gamma^{1/2}$.

TABLE I. Triple-point viscosities and Lyapunov exponents. η_L is the viscosity computed using Eq. (11). $\eta_{\rm NEMD}$ is the NEMD viscosity, determined directly from the NEMD simulation. $N=108$ or 864 as indicated, $n=0.8442$, $e=E/N\epsilon=1.930\,19$, WCA potential. The variation in temperature is due to the constant energy condition. $\gamma=1$ corresponds to a Péclet number ~ 5. η_L (error) is the estimated uncertainty in η_L. The uncertainty in $\eta_{\rm NEMD}$ is relatively insignificant.

γ	$T_{\rm SS}$	$\eta_{\rm NEMD}$	η_L	$\lambda_{\rm max}$	$-\lambda_{\rm min}$	η_L (error)
			$N=108$			
0.35	0.7623	2.053	2.03	4.1938	4.0647	0.04
0.5	0.7563	1.961	1.92	4.3061	4.0555	0.04
0.75	0.7412	1.883	1.86	4.545	3.9874	0.04
1.0	0.7236	1.783	1.77	4.8732	3.9097	0.027
			$N=864$			
0.5	0.756	1.984	2.02	4.28	4.017	0.15
0.75	0.743	1.887	1.94	4.51	3.93	0.20
1.0	0.7218	1.749	1.74	4.8298	3.88	0.1

the agreement between η_L and $\eta_{\rm NEMD}$ is within estimated statistical uncertainties ($\pm 5\%$) for all shear rates studied. Because the shear induced shift in the Lyapunov exponents is asymptotically quadratic in the strain rate, the Lyapunov method becomes very difficult at small shear rates.

The $N=108$, NEMD data for $\eta_{\rm NEMD}(\gamma)$ and $\eta_L(\gamma)$ as a function of γ can be fitted to the equation

$$\eta(\gamma)=\eta(0)-A\gamma^{1/2}\,, \tag{28}$$

where one has, for $\eta_{\rm NEMD}$, $\eta_{\rm NEMD}(0)=0.402$ and $A_{\rm NEMD}=0.087$, while for η_L one has $\eta_L(0)=0.384$ and $A_L=0.074$, respectively.

Table I shows a comparison of $\eta_{\rm NEMD}(\gamma)$ and $\eta_L(\gamma)$ for a WCA fluid close to the Lennard-Jones triple point, with $e=1.930\,19$ and $n=0.8442$ for both $N=108$ and 864. Figure 5 gives a comparison of the $N=108$ viscosities at this state point. As can be seen the Lyapunov and the NEMD data are in excellent ($\pm 2\%$) agreement with each other for all γ. At this state point the viscosity is approximately five times larger than at the lower density state point. This improvement in the signal-to-noise ratio enabled us to continue the calculations and make comparisons at smaller shear rates than was possible at $n=0.4$.

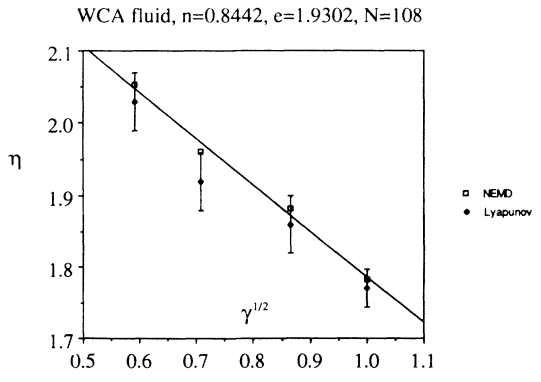

FIG. 5. We make a comparison of Lyapunov and NEMD shear viscosities for a dense fluid state point: $e=1.9302$ and $n=0.8442$, $N=108$. Both sets of data are in agreement and are consistent with a linear dependence on $\gamma^{1/2}$, indicated by the straight line.

The coefficients for the fit to the square-root functional form (28) are $\eta_{\rm NEMD}(0)=2.425$, $A_{\rm NEMD}=0.639$, and $\eta_L(0)=2.37$, $A_L=0.601$. All these values are again consistent with each other within the experimental uncertainties. Table I also shows a limited set of $N=864$ results. It is clear from these data that as expected,[19] there is only a slight number dependence in $\eta_{\rm NEMD}(\gamma)$ in going from $N=108$ to 864. The results suggest that for large enough N, not only is $\eta_L(\gamma)$ and therefore $\lambda_{\rm max}+\lambda_{\rm min}$, independent of N, but, as in the FPU system,[9] $\lambda_{\rm max}$ and $\lambda_{\rm min}$ also appear to be independent of N.

We should comment that while in this paper we compare $\eta_L(\gamma)$ with $\eta_{\rm NEMD}(\gamma)$, we know from previous studies that extrapolation to $\gamma=0$, via the square-root expression, (28), yields excellent agreement[19] with estimates of $\eta(0)$, obtained from the Green-Kubo formulas.

VII. DISCUSSION

We end with the following remarks.

(1) The basic relation (11) between the viscosity η and the sum of the two maximal Lyapunov exponents allows not only a computation of η from the maximum and minimum Lyapunov exponents but holds for any conjugate pair of Lyapunov exponents. In addition it also holds for the perturbed equilibrium zero-valued Lyapunov exponent $\bar{\lambda}$ in that $\langle\alpha\rangle=-2\bar{\lambda}$, connecting the shift of the zero eigenvalue for $\gamma=0$, and the coupling constant of the fluid to the heat bath.

(2) Equation (11) also provides information about the dependence of the Lyapunov exponents on the state of the system in the stationary state. In fact, since for $\gamma=0^+$, the (linear) shear viscosity η for a dilute gas is independent of the density,[20] $\lambda_i+\lambda_{i'}$ must be inversely proportional to the density. Similarly, for a dilute gas of hard spheres, $\lambda_i+\lambda_{i'}\sim T^{1/2}$, since this holds for η.[20] One

could wonder whether this density and temperature dependence are also obtained for the individual Lyapunov exponents λ_i. Also, as one approaches the glass transition, $\lambda_i + \lambda_{i'}$ must diverge.

(3) The Lyapunov sum rule and the conjugate pairing rule show that Lyapunov instability and chaotic dynamics are relevant for the understanding of nonequilibrium processes and the calculation of transport coefficients. In fact the existence of Lyapunov exponents in the contracting phase space of thermostatted dissipative systems is intimately related to the very existence of transport coefficients.

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