

Viscous flow in the stress ensemble†

by DENIS J. EVANS‡ and JAMES F. ELY

Thermophysics Division, National Engineering Laboratory,
National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

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The stress ensemble has advantages for studying shear flow in highly viscous media. We derive a simple method for performing nonequilibrium molecular dynamics simulations in this ensemble. We also derive the associated equilibrium fluctuation expressions for the zero frequency shear viscosity. These expressions relate the reciprocal of the shear viscosity to strain rate fluctuations in the zero stress equilibrium ensemble. Our analysis is based upon the Nosé-Hoover method of treating non-holonomic constraints. We show that for generating the stress ensemble, the Nosé-Hoover method is much simpler to implement than the corresponding gaussian approach.

1. INTRODUCTION

In conventional nonequilibrium molecular dynamics (NEMD) simulations of shear flow in fluids, one solves the Sllod equations of motion for a periodic system of N particles under shearing boundary conditions [1, 2]. The equations of motion are

$$\dot{\mathbf{r}}_j = \frac{\mathbf{p}_j}{m} + \gamma \hat{\mathbf{i}} y_j$$

and

$$\dot{\mathbf{p}}_j = \mathbf{F}_j - \gamma \hat{\mathbf{i}} p_{yj} - \alpha \mathbf{p}_j, \quad 1 \leq j \leq N, \quad (1)$$

where $\hat{\mathbf{i}}$ denotes a unit vector in the x -direction, \mathbf{p}_j and \mathbf{r}_j are the momentum and position of the j th molecule, m is the mass and \mathbf{F}_j is the force on j . In equation (1) α is a thermostating parameter and when

$$\alpha = \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j - \gamma \sum_j p_{xj} p_{yj}}{\sum_j \frac{p_j^2}{m}}, \quad (2)$$

the temperature, as determined from the peculiar kinetic energy, is a constant of the motion. Evans and Morriss [2] have recently proved that these equations give an exact description of isothermal planar Couette flow at a strain rate, $\partial u_x / \partial y = \gamma$.

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‡ Permanent address to which all correspondence should be sent: Research School of Chemistry, Australian National University, GPO Box 4, Canberra ACT, 2601, Australia.

It has also been shown that (1) and (2) give the correct description of nonlinear effects such as shear thinning and shear dilatancy as well as time dependent viscoelastic phenomena.

If one wants to simulate the rheology of a Bingham plastic these equations of motion have disadvantages. It would be more convenient to have the shear stress as an independent variable rather than the strain rate. This would for example, permit the direct determination of the yield stress for Bingham plastics.

Such a simulation would be an example of a Norton ensemble calculation [3], because by analogy with electric circuit theory, the thermodynamic flux rather than the force would be the independent state defining variable. From a formal statistical mechanical viewpoint, little is known about transport theory in the Norton ensemble. For example Green–Kubo (GK) relations are always derived in a force or Thevenin ensemble. An exception to this is our recent derivation of the GK expression for the resistance of a Norton circuit [3]. The result of that study was the derivation of the thermodynamic conjugate of the Kubo expression for the conductivity of the corresponding Thevenin circuit.

Recently, Brown [4] has used gaussian methods [1] to perform simulations at constant shear stress. In addition, Parrinello and Rahman [5] have studied the constant stress ensemble at constant enthalpy to obtain expressions for the elastic compliances of crystals. Of particular interest in this work are Brown's equations of motion which were derived by treating the strain rate in (1) and (2) as a Lagrange multiplier which is chosen from the condition that the shear stress is constant [1, 4]. This was precisely the method used by Evans and Morriss [1] to develop isothermal/isobaric equations of motion. Brown's expression for the strain rate which is given in the Appendix is quite complex, making it extremely difficult to analyse theoretically. In this paper we develop a simpler scheme which allows the stress to fluctuate about a specified mean value. The nature of these fluctuations results in major simplifications in the mathematical analysis. The price paid for these simplifications is that the method only works at zero frequency.

2. THE NOSE–NORTON STRESS ENSEMBLE

In 1984 Nosé [6] proposed a constant temperature simulation algorithm based on Anderson's method for controlling the pressure [7]. The difference between Nosé's method and the gaussian thermostating method of Hoover and Evans [8, 9] is that in gaussian methods, the peculiar kinetic energy is a constant of the motion while in the Nosé method the peculiar kinetic energy fluctuates about a specified mean value. Recently, Hoover [10] proposed significant simplifications in the implementation of the Nosé thermostat. We shall use the Hoover form of Nosé dynamics in this paper although similar results may be obtained starting with the Anderson–Parrinello–Rahman formalism [5, 7]. In particular, we shall use the basic idea of the Nosé–Hoover (NH) thermostat to drive a system away from equilibrium. Consider the equations of motion,

$$\dot{\mathbf{r}}_j = \frac{\mathbf{p}_j}{m} + \hat{\mathbf{i}}\gamma y_j, \quad (3)$$

$$\dot{\mathbf{p}}_j = \mathbf{F}_j - \hat{\mathbf{i}}\gamma p_{y_j} - \zeta \mathbf{p}_j, \quad (4)$$

$$\dot{\gamma} = \frac{1}{Q_\gamma} (P_{xy}V - S_{xy}V), \quad (5)$$

$$\dot{\xi} = \frac{1}{\tau^2} \left(\frac{K}{K^0} - 1 \right), \quad (6)$$

where V is the volume, $-P_{xy}$ and $-S_{xy}$ are the instantaneous and desired shear stresses, τ is a relaxation time, K denotes the instantaneous kinetic energy and K^0 is the desired kinetic energy determined from the desired temperature via $K^0 = 3NkT/2$.

Equations (3) and (4) are identical to the isothermal Slrod equations for shear flow given in (1) above. What is different about these equations is that the strain rate γ is not an independent state variable, but rather satisfies a differential equation which relates the rate of change of γ to the degree to which the instantaneous shear stress, $-P_{xy}$ differs from a specified value, $-S_{xy}$. If the instantaneous stress is greater than the specified value, the strain rate will decrease in an attempt to make the two stresses more nearly equal.

A second difference in these equations from (1) and (2) is that we are now employing the NH thermostat rather than a gaussian one. Properties of the NH thermostat are reasonably well understood [9]. It should be noted, however, that the relaxation time, τ , should be chosen to correspond to some microscopic relaxation time, otherwise the resulting equations of motion will be stiff [11].

Since the time derivative of the internal energy, $H = \sum p_j^2/2m + \Phi$ is given by

$$\dot{H}_0 = -P_{xy}\gamma V - 2\xi K, \quad (7)$$

the dynamics described by (3)–(6) do not satisfy the Liouville equation. Instead they satisfy a Non-Liouville equation in which phase space behaves as a compressible $6N + 2$ dimensional fluid [1, 11]. The N -particle distribution function f^N is a function of the $6N$ particle positions and momenta, the thermostat multiplier ξ , and the strain rate γ , viz., $f^N = f^N(\Gamma, \xi, \gamma)$ where $\Gamma = \{\mathbf{r}_1, \dots, \mathbf{p}_N\}$. The non-Liouville equation is

$$\frac{\partial f^N}{\partial t} = -\dot{\Gamma} \cdot \frac{\partial f^N}{\partial \Gamma} - \xi \frac{\partial f^N}{\partial \xi} - \dot{\gamma} \frac{\partial f^N}{\partial \gamma} - f^N \left[\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \frac{\partial \xi}{\partial \xi} + \frac{\partial \dot{\gamma}}{\partial \gamma} \right]. \quad (8)$$

Since $\xi = \xi(\Gamma)$ and $\dot{\gamma} = \dot{\gamma}(\Gamma)$, $\partial \xi / \partial \xi = \partial \dot{\gamma} / \partial \gamma = 0$. Using the equations motion $(\partial / \partial \Gamma) \cdot \dot{\Gamma}$ is easily seen to be $-3N\xi$.

When the set value of the shear stress, $-S_{xy}$, is zero, elementary principles of statistical mechanics give the equilibrium distribution function [1] as

$$f_0^N = \frac{\exp -\beta[H_0 + \frac{1}{2}Q_\gamma\gamma^2 + \frac{1}{2}Q_\xi\xi^2]}{\int d\Gamma \int d\gamma \int d\xi \exp -\beta[H_0 + \frac{1}{2}Q_\gamma\gamma^2 + \frac{1}{2}Q_\xi\xi^2]}, \quad (9)$$

where

$$Q_\xi = 3NkT\tau^2 = 2K^0\tau^2$$

and

$$\beta = 3N/2K^0 = 1/kT.$$

That this solution is correct is easily checked by substitution into the non-Liouville equation. This shows, using (7), that $\partial f_0^N / \partial t = 0$. The equilibrium distribution function is thus a generalized canonical distribution permitting strain rate fluctuations,

$$\langle \gamma^2 \rangle_{S_{xy}=0} = \frac{kT}{Q_\gamma}. \quad (10)$$

These strain rate fluctuations are unphysical since their amplitude is controlled by the adjustable constant Q_γ .

3. LINEAR RESPONSE THEORY

Suppose we subject an equilibrium ensemble of systems, characterized by the distribution f_0^N , to an externally imposed stress, $-S_{xy}$. It is now a simple matter to apply the results of the linear response theory of Evans and Holian [11] to this problem. The fact that the external field is a flux causes no difficulties because it appears explicitly in the equations of motion. This is in contrast to the much more difficult case of applying gaussian methods to the Norton ensemble [4]. In that case it is not usually possible to express the equations of motion in a form where the set value of the thermodynamic flux appears explicitly. A second difficulty of using gaussian methods for generating the Norton ensemble is, that except in simple cases [3], the AIF condition [1] is not satisfied. From Brown's gaussian equations of motion [4], it would appear that the calculation of the required phase space compression factor, $(\partial/\partial\Gamma) \cdot \Gamma$, would be exceedingly complex. Using our equations of motion under adiabatic conditions ($\xi = 0$) there are no such difficulties since AIF is satisfied. From (7) we see that the adiabatic derivative of the extended internal energy, $E = H_0 - Q_\gamma \gamma^2$, is

$$\dot{E}^{\text{ad}} = -S_{xy} V \dot{\gamma}. \quad (11)$$

Applying the results of Evans and Holian [11] we find that

$$\langle \gamma(t) \rangle_{S_{xy}} = \int_0^t \chi(s) S_{xy} ds + O(S_{xy}^2) \quad (12)$$

where the Norton ensemble susceptibility, χ , is

$$\chi(t) = -\beta V \langle \dot{\gamma}(0) \gamma(t) \rangle_{S_{xy}=0}. \quad (13)$$

This expression shows that the shear viscosity, η , is given by

$$\eta = 1 \left/ \int_0^\infty dt \beta V \langle \dot{\gamma}(0) \gamma(t) \rangle_{S_{xy}=0} \right. \quad (14)$$

which is the Norton conjugate of the usual Green-Kubo result obtained in the Thevenin ensemble

$$\eta = \int_0^\infty dt \beta V \langle P_{xy}(0) P_{xy}(t) \rangle_0. \quad (15)$$

Comparison of Norton and Thevenin ensembles for shear flow.

γ^*	$-P_{xy}^*$	P_{xx}^*	P_{yy}^*	P_{zz}^*	<i>kts</i>	Ensemble
0.2	0.55 ± 0.01	0.98 ± 0.03	1.06 ± 0.03	0.96 ± 0.02	50	<i>T</i>
0.20 ± 0.01	0.57	0.95 ± 0.02	1.07 ± 0.03	0.95 ± 0.02	50	<i>N</i>
1.0	2.09 ± 0.02	2.02 ± 0.05	2.03 ± 0.02	1.58 ± 0.01	18	<i>T</i>
1.02 ± 0.02	2.07	1.98 ± 0.02	2.06 ± 0.02	1.58 ± 0.02	15	<i>N</i>
2.0	3.18 ± 0.06	3.26 ± 0.01	3.37 ± 0.07	2.53 ± 0.03	25	<i>T</i>
1.94 ± 0.06	3.18	3.24 ± 0.02	2.42 ± 0.02	2.51 ± 0.04	10	<i>N</i>

kts = 1000 time steps, *T* = Thevenin, *N* = Norton.

Our Norton ensemble result is however less general than the usual Thevenin expression because it cannot easily be generalized to non-zero frequencies. In particular, the frequency dependent shear viscosity is not given by the reciprocal of the Fourier–Laplace transform of the strain rate autocorrelation function. At infinite frequencies (10) shows that such an approach is dominated by the Nosé time constant rather than by the infinite frequency shear modulus. Gaussian methods of generating the Norton ensemble do not suffer from this defect [3].

4. NUMERICAL RESULTS

We decided to perform a computer ‘experiment’ to verify the thermodynamic equivalence of the Thevenin and Norton ensembles, as we have defined them for shear flow. Non-equilibrium molecular dynamics simulations were run for planar Couette flow in the triple point Lennard-Jones fluid. The equivalence test was performed for shear rates which span a range of nonequilibrium behaviour from the linear, Newtonian regime far into the non-linear, non-Newtonian region.

Intermolecular interactions were truncated at $r^* = 2.5$. All units are reduced with respect to the molecular interaction parameters, m , ϵ , σ . In both the Thevenin and Norton ensemble calculations, the gaussian thermostat was used to control the temperature at the equilibrium triple point value of $T^* = 0.722$. The gaussian thermostat was used because of its greater computational efficiency compared to the Nosé–Hoover thermostat [10]. The density was set at the Lennard-Jones equilibrium triple point value of $\rho^* = 0.8442$.

Thevenin ensemble calculations were performed first so that the Thevenin averaged shear stress could be used as input to the corresponding Norton ensemble calculation. The value chosen for the constant Q_γ was 0.2. The results are tabulated above. It is clear that within statistical uncertainties, the results are independent of whether they are determined from simulations at constant applied strain rate—Thevenin ensemble—or at specified mean shear stress—Norton ensemble. This equivalence is apparent even when the system is far from equilibrium $\gamma^* = 2$, where the hydrostatic pressure is many times greater than it is at equilibrium.

These results provide an ‘experimental’ confirmation that the equivalence of gibbsian equilibrium ensembles can be extended to nonequilibrium steady states. The response theory outlined in §3 provides a basis for understanding linear transport processes in Norton ensembles. It is clear that these methods can be simply extended to each of the other Navier–Stokes transport processes.

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APPENDIX

Brown's equations of motion

In applying gaussian techniques to the constant stress ensemble, one requires the rate of change of the xy component of the stress to be a constant. Differentiating this quantity with respect to time yields

$$-V\dot{S}_{xy} = \frac{1}{m} \sum_j (\dot{p}_{x_j} p_{y_j} + p_{x_j} \dot{p}_{y_j}) + \sum_j (\dot{x}_j F_{y_j} + x_j \dot{F}_{y_j}),$$

where V is the volume of the system. Substituting for \dot{p} , \dot{x} , and α from equations (1) and (2) and assuming the potential to be pairwise additive one finds for γ appearing in equations (1) and (2)

$$\gamma = \frac{L_1 - L_2 + \dot{S}_{xy}V}{L_3 + L_4},$$

where the sums $L_1 - L_4$ are given by the following

$$L_1 = \frac{1}{m} \sum_j \left[2p_{x_j} F_{y_j} + F_{x_j} p_{y_j} - 2(\mathbf{p}_j \cdot \mathbf{F}_j) \left(\frac{\sum_i p_{x_i} p_{y_i}}{\sum_k \mathbf{p}_k^2} \right) \right],$$

$$L_2 = \frac{1}{m} \sum_i \sum_j \frac{x_{ij}}{|\mathbf{r}_{ij}|} [p_{y_{ij}} \phi'_{ij} + (\mathbf{r}_{ij} \cdot \mathbf{p}_{ij}) y_{ij} (\phi''_{ij}/|\mathbf{r}_{ij}| - \phi'_{ij}/r_{ij}^2)],$$

$$L_3 = \frac{1}{m} \sum_j p_{y_j}^2 - \frac{2}{m} \left[\sum_j p_{x_j} p_{y_j} \right]^2 / \sum_j \mathbf{p}_j^2,$$

$$L_4 = \sum_i \sum_j \frac{x_{ij}^2 y_{ij}^2}{\mathbf{r}_{ij}^2} [\phi''_{ij} - \phi'_{ij} \cdot (1 - \mathbf{r}_{ij}^2/x_{ij}^2)/|\mathbf{r}_{ij}|],$$

where m is the mass of a particle and ϕ_{ij} is the interaction potential between particles i and j .

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