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Rheology and Thermodynamics from Nonequilibrium Molecular Dynamics[1]

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We review some of the recent developments in nonequilibrium molecular dynamics (NEMD) simulations of fluids. One of the areas which has been profoundly influenced by this new technique is the study of systems undergoing steady planar Couette flow. Attention has been focused on developments which have taken place since the 1982 Conference on Nonlinear Fluid Behaviour. Since that time many questions concerning the formal justification of NEMD algorithms have been successfully answered. There have also been extensions of the range of properties studied by the technique.

KEY WORDS: algorithms; Couette flow; nonequilibrium molecular dynamics; nonlinear fluid behavior; rheology; simulation.

1. INTRODUCTION

In this review, we concentrate on developments that have taken place since the 1982 Conference on Nonlinear Fluid Behavior [1]. At that time, NEMD simulations of planar Couette flow had revealed that even simple atomic fluids can, under suitable conditions, exhibit a wide variety of non-Newtonian behavior. The Lennard–Jones fluid had been shown to be viscoelastic, shear thinning, and capable of displaying normal stress effects [2]. All of these properties are well-known, experimentally observable effects in molecularly complex non-Newtonian fluids. The simulations also revealed an associated property which is almost impossible to observe experimentally, namely, shear dilatancy—the expansion of fluids with increasing shear rate under isothermal isobaric conditions. Before the

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advent of NEMD, some rheologists had fallen into the habit of assuming that shear thickening and shear dilatancy always accompanied each other [3]. The two terms had been widely confused in the literature. NEMD proved that the effects were distinct by showing that atomic fluids were shear *thinning* but dilatant.

By 1982, NEMD simulations had shown that the non-Newtonian dispersion relations were apparently nonanalytic [1, 2], the first correction to Newtonian constitutive relations typically depending upon the square root of the strain rate. At first this observation was received with some joy because the analytic form for these non-Newtonian constitutive relations was is agreement with the predictions of mode coupling theory [4–7]. However, this happy circumstance was short-lived when it was realized that the observed size of these effects was orders of magnitude larger than theoretical predictions [2, 8].

At this time, a number of doubts were raised as to the validity of the NEMD algorithms themselves [1]. In 1982, the formal basis of NEMD simulations was poorly understood. This is one of the main themes of the present paper. We summarize the presently understood basis of NEMD, including such matters as the theory of thermostats as well as the formulation of equations of motion which will efficiently and correctly drive a hydrodynamic flow.

We also summarize some of the results of new NEMD simulations which have been performed which might help to shed light on the basic dilemma in this field: Why is it that simulation agrees with mode-coupling functional forms for nonlinear constitutive relations but is in major disagreement as to the amplitudes of these effects?

The last matter that we discuss is the role played by nonlinear irreversible thermodynamics in trying to understand nonequilibrium steady states far from equilibrium. In contrast to mode-coupling theory, this extended thermodynamics has led to *quantitatively accurate* predictions of some of the properties of steady states. In particular, this theory has derived apparently correct expressions for the interrelations among isobaric shear dilation, the shear-induced, isochoric increase in pressure, the shear-induced decrease in temperature in steady states with the same internal energy, and the increase in the specific heats with shear rate. Thermodynamics has important consequences for the stability of shear flow at low shear rates in two-dimensional systems.

2. THEORY OF ALGORITHMS

In 1982, there were two algorithms that had been developed to drive shear flow, the homogeneous shear method [9] and the Dolls tensor algorithm [10]. The homogeneous shear method was basically an adaption of periodic boundary conditions to shear flow. The Dolls tensor method, on the other hand, employed a fictitious external field to drive the flow. However, it still employed time-varying periodic boundary conditions. The Dolls tensor method could be proved to yield the correct behavior close to equilibrium using linear response theory [10]. Further from equilibrium both methods seemed to yield consistent results but there was no proof of the correctness of the Dolls tensor method in this regime.

By 1982, Hoover et al. [11] and Evans [12] had realized how to formulate equations of motion for which the temperature or the internal energy is a constant of the motion. These equation could be used in equilibrium and nonequilibrium simulations. However, at that time no theory existed which could escribe the thermostate response of nonequilibrium systems. The isothermal equations of motion for a field-free system are

$$\begin{aligned} d\mathbf{q}/dt &= \mathbf{p}/m \\ d\mathbf{p}/dt &= \mathbf{F} - \alpha\mathbf{p} \end{aligned} \tag{1}$$

where

$$\alpha = \sum \mathbf{F}\cdot\mathbf{p}/\sum p^2 \tag{2}$$

In a series of papers Evans and Morriss [13–15] developed a formal theory of the dynamical behavior of thermostatted systems. They showed by Dyson decomposition techniques that equilibrium time correlation functions for the Navier–Stokes transport coefficients are in the thermodynamic limit, independent of whether the dynamics is generated by Newtonian equations of motion or the so-called "Gaussian isothermal" equations of motion [14].

In 1984, Nose proposed an alternative dynamics [16, 17] which permits fluctuations in the system kinetic energy. Nose showed that at equilibrium, in an ergodic system, his dynamics generates the canonical ensemble. The field-free equilibrium distribution function for isothermal dynamics is, in contrast, the isothermal distribution f_{T} [14],

$$f_{\mathrm{T}} = \delta(K - K_0)\exp(-\beta\Phi)\bigg/\int d\Gamma\,\delta(K - K_0)\exp(-\beta\Phi)$$

where K and Φ are the kinetic and potential energies, and

$$\beta = 3N/(2K_0) \tag{3}$$

In 1985, Hoover [18] reformulated the Nose system of dynamics in a form which is much more suitable for computer simulation. In the form derived by Hoover, the equations are suitable for thermostating nonequilibrium systems. In field-free conditions, the Nose–Hoover (NH) equations are

$$\begin{aligned} d\mathbf{q}/dt &= \mathbf{p}/m \\ d\mathbf{p}/dt &= \mathbf{F} - \xi\mathbf{p} \end{aligned} \tag{4}$$

where

$$\xi = (K/K_0 - 1)/\tau$$

τ is an undetermined time constant which controls the time scale of kinetic energy fluctuations. It should be chosen to match a microscopic relaxation time, otherwise the NH equations of motion will be "stiff" [19].

Very recently, Evans and Holian [19] have proved that in the thermodynamic limit, equilibrium time correlation functions formed under NH dynamics, Gaussian isothermal dynamics, or Newtonian dynamics are all equivalent. Knowing the relations between equilibrium time correlation functions is important because it allows one to compare the thermostatted linear response of systems to an external field. Holian and Evans also showed that although NH dynamics is often convenient for theoretical analysis, it appears to be considerably less efficient and accurate in simulations than are the Gaussian schemes. To achieve a comparable accuracy in viscosity calculations, for example, they found that even when the choice of τ was optimal, NH dynamics consumed four times as much computer time as did the corresponding Gaussian isothermal method [19].

The generalization of linear response theory to thermostatted systems is not straightforward [20]. This is because in the presence of a thermostat, the usual form of the Liouville equation is not valid. The Liouville operator itself turns out to be non-Hermitian, Morriss and Evans succeeded in calculating the linear response of Gaussian isothermal systems [15]. The resultant susceptibility is formally identical to the adiabatic case except that the time evolution is generated by the field-free isothermal equations of motion. It takes the form of an isothermal equilibrium time correlation function. Similarity if an external field is applied to a system thermostated by the NH thermostat, the linear response is determined by a field-free equilibrium time correlation function generated under NH dynamics. Since both of these equilibrium time correlation functions are equivalent in the thermodynamic limit and, of course, equal to the corresponding Newtonian correlation function, we know that in the linear regime at least, the response is independent of the thermostatting mechanism [15].

The general procedure [20, 21] for generating an NEMD algorithm is to devise an external field and, in particular, its coupling to the system of interest, so that for a chosen phase variable the susceptibility to the external field matches the Green–Kubo relation for the desired thermal transport coefficient. This has proven to be the most efficient, number-independent way of calculating thermal transport coefficients such as viscosity and thermal conductivity [22]. This procedure does not uniquely define an NEMD algorithm for a given thermal transport coefficient. There are many synthetic external fields capable of generating a specific *linear* susceptibity. The procedure also does not usually result in equations of motion which can be generated from a Hamiltonian. The adiabatic forms of the favored algorithms for shear viscosity and thermal conductivity cannot be generated from Hamiltonians [20].

In spite of this, one property of Hamiltonian dynamics is usually preserved. In the absence of thermostats, the equations of motion preserve phase space ($df/dt = 0$). This condition is called the adiabatic incompressibility of phase space, $AI\Gamma$ [19–21].

The linear theory of NEMD seems to be essentially complete. In the nonlinear domain our knowledge is much more rudimentary. There are no known analogues of the Green–Kubo relations for any of the Navier–Stokes transport coefficients in the nonlinear domain. Nonlinear response theory seems to lead to many as yet unresolved difficulties [15, 23]. In spite of these difficulties, we know that two forms of the so-called SLLOD algorithm for viscosity are exact arbitrarily far from equilibrium [24]. This is due to the high degree of symmetry of planar Couette flow. The SLLOD equations of motion for isothermal planar Couette flow, $\partial u_x/\partial y = \gamma$, are

$$\begin{aligned}
\dot{x} &= p_x/m + \gamma y \\
\dot{y} &= p_y/m \\
\dot{z} &= p_z/m \\
\dot{p}_x &= F_x - \gamma p_y - \alpha p_x \\
\dot{p}_y &= F_y - \alpha p_y \\
\dot{p}_z &= F_z - \alpha p_z
\end{aligned} \tag{5}$$

where the thermostating multiplier α is

$$\alpha = \left(\sum \mathbf{F} \cdot \mathbf{p} - \gamma \sum p_x p_y \right) \Big/ \sum p^2 \tag{6}$$

As mentioned above, these equations must be implemented under the usual periodic shearing boundary conditions for shear flow. It is a simple matter to modify these equations for flow deformations other than planar Couette. The momenta **p** appearing in these equations are measured relative to the local streaming velocity in the fluid. This is a considerable convenience for calculating thermodynamic properties. The thermostatting multiplier can be chosen so that the thermodynamic internal energy of the system is a constant of the motion. In proving that the SLLOD algorithm gives an exact description of shear flow far from equilibrium, Evans and Morriss [24] also showed that the Dolls tensor method is incorrect at second order in the shear rate.

New and interesting results concerning the nonlinear behavior of gases composed of periodic images of two hard spheres have been derived by Hoover [25] and Morriss [26]. Although comparatively simple, the thermostatted response of this system can be calculated analytically. It is hoped that when analyzed, this system may serve as a guide to developing a useful theory of the nonlinear response.

3. NEMD SIMULATION RESULTS

By 1982, it was established that both shear viscosity and bulk viscosity exhibit what are known as "enhanced long-time tail behavior" [2, 10]. A summary of these is given in Table I. Although the early results were obtained using what we would now refer to as primitive algorithms, subsequent refinements of techniques have not basically altered the conclusions. For example, prior to 1982, all thermostatting was done by ad hoc rescaling [9] of the second moment of the velocity distribution at every time step during the course of the simulation. Repeating these calculations using Gaussian or NH thermostats leads to essentially identical results [12, 19].

The calculations of shear thinning behavior have been extended to four dimensions, leading to the same puzzle as did the earlier results in lower dimensionality—agreement with the mode-coupling functional forms but massive disagreement on amplitudes [27]. In 1983, Evans and Gaylor [28] showed that the second rank-order tensor in a diatomic molecular fluid also appears to exhibit enhanced long-time tail effects. This calculation is important for two reasons. First, it demonstrates that enhanced long-time tail behavior can be seen from simulations which employ fixed orthogonal periodic boundaries. For both viscosities the NEMD simulations must be carried out using time-varying periodic boundaries, and it had been suggested that they may have been creating spurious effects. Second, this calculation shows that whatever is responsible for these "enhanced" effects it is capable of coupling to other macroscopic properties of suitable tensorial character.

In this connection, NEMD simulations have now been carried out for all the Navier–Stokes transport coefficients—shear and bulk viscosity, ther-

Table I. Limiting Behavior of Non-Newtonian Constitutive Relations[a]

$d = 2$

$$\eta(\gamma) = -A \log(B\gamma)$$
$$p(\gamma) = p(0) + A\gamma \log(B\gamma)$$
$$E(\gamma) = E(0) + A\gamma \log(B\gamma)$$

$d = 3$

$$\eta(\gamma) = \eta(0) - A\sqrt{\gamma}$$
$$p(\gamma) = p(0) + A\gamma\sqrt{\gamma}$$
$$E(\gamma) = E(0) + A\gamma\sqrt{\gamma}$$
$$\eta(\omega) = \eta(0) - A\sqrt{\omega}$$
$$\eta(k) = \eta(0) - Ak\sqrt{k}$$

$d = 4$

$$\eta(\gamma) = \eta(0) - A\gamma$$
$$p(\gamma) = p(0) + A\gamma$$
$$E(\gamma) = E(0) + A\gamma$$

[a] All results pertain to the limiting behavior as γ, ω, k tend to zero. Thermodynamic instabilities prevent the observation of the logarithmic divergence of η in two dimensions. For shear rates less than the critical value at which shear dilatancy would become negative, an apparently "Newtonian" regime is entered in which the planar velocity itself is unstable. The four-dimensional result for η is as expected from mode-coupling theory, however, the pressure and energy exponents, which had always been one order greater in γ (see two and three dimensions for comparison), are unusual. Thermodynamics predicts that the pressure exponent must be less than 2, independent of the dimensionality.

mal conductivity, and self-diffusion [29]. When using reasonably accurate interaction potentials, all calculations yield predicted transport coefficients which agree with experiment within statistical uncertainties. These calculations also show that enhanced long-time tail behavior seems confined to the viscosities (and related transport coefficients as mentioned above). It seems clear that these "enhancements" are somehow related to the glass transition. If a transport coefficient diverges at that transition, it will, in all probability, exhibit enhanced behavior. Recently, Keyes [30] has used these ideas in a scaling theory of the long-time tail. He has suggested that the reason the shear viscosity diverges at the glass transition is precisely because the amplitudes of the long-time tails diverge there. Unfortunately, there are severe difficulties in performing NEMD simulations of shear viscosity within the metastable fluid region of the phase diagram. It is difficult to perform direct checks of Keyes' ideas using conventional simulation methods.

There has also been interest in flows at very high shear rates. By "very high" we mean shear rates so high that the flows become athermal, with temperature ceasing to have much significance for the nature of the flow. Under these extreme conditions, Erpenbeck [31] discovered that fluids enter an ordered phase with particles "slip-streaming" into strings to minimize the entropy production. This is an example of a shear-induced phase change.

This was not the first shear-induced phase change to be observed. In 1982, we [32] noticed that crystals could be forced to melt by shearing while maintaining the system at a temperature and density at which a crystaline phase would be stable if the system were at equilibrium. This observation from NEMD simulations seemed to be an exact analogue of the experimental observation of shear-induced melting by Clark and Ackerson [33].

NEMD techniques have advanced to such a degree that we are beginning to see the results of simulations for molecularly complex materials. The generalization of the methods to polyatomic fluids is relatively straightforward [34, 35]. Early simulations on shear flow in a diatomic liquid were carried out in 1981 [36], while Brown and Clarke have performed calculations for hexane [37].

4. THERMODYNAMIC PREDICTIONS

In 1980, Hanley and Evans [38–40] developed an extension of thermodynamics applicable to shearing, nonequilibrium steady states. They postulated that, outside the linear regime, thermodynamic potentials depend upon the magnitude of the thermodynamic driving force in addition to the usual equilibrium state variables, temperature and density. These ideas were not new, being almost as old as thermodynamics itself. In more recent times, much of the formal development of extended irreversible thermodynamics has been carried out by Peacock-Lopez and Keizer [4] and Lebon et al. [42]. For planar Couette flow, the generalized first law was postulated to be

$$dE = dQ - p\, dV + \zeta\, d\gamma \tag{7}$$

The second law was postulated to be

$$dQ \geqslant T\,dS \tag{8}$$

The entropy of the system S, like the internal energy E, can be considered to be functions $S(N, T, V, \gamma)$ and $E(N, T, V, \gamma)$. From these apparently simple postulates, a wealth of interrelationships can be derived. One of these "Maxwell" relationships was subjected to an accurate test by Evans [12] in 1983. In performing this test the newly developed refinements to NEMD were essential. Evans verified, by computer experiment, the thermodynamic prediction that

$$dT/d\gamma)_{E,V} = -dE/d\gamma)_{T,V} 1/C_{V,\gamma} \tag{7}$$

where the specific heat at fixed volume and strain rate, $C_{V,\gamma}$, is defined in the usual way as

$$C_{V,\gamma} = dE/dT)_{V,\gamma} \tag{8}$$

NEMD simulations were performed to calculate all derivatives numerically. The specific heat as a function of the shear rate was measured from simulation data. These data were combined with measured data for $dT/d\gamma)_{E,V}$ to predict $E(\gamma)$ at fixed temperature and volume. This prediction agreed with subsequent NEMD simulation results for $E(\gamma)$, within estimated statistical uncertainties. The calculations required extreme precision. The maximum shear-induced energy change was only 5.6% of the equilibrium value of the energy. In spite of this small excess energy, the maximum disagreement between the thermodynamic prediction for the excess energy and that observed in NEMD was less than 2% of the excess energy. NEMD thus confirmed to high accuracy the thermodynamic prediction that the temperature of a shearing system *drops* as the shear rate is increased while keeping the volume and internal energy fixed. To our knowledge this is the first time that there has been a quantitative test of any of the predictions of nonlinear irreversible thermodynamics.

Thermodynamic stability theory makes a number of predictions concerning the sign of second-order thermodynamic quantities. For a steady state to be stable the specific heat must, of course, be positive. $dp/dV)_{T,\gamma}$ must be negative and $d\zeta/d\gamma)_{T,V}$ must be positive. The latter condition will always be satisfied if a fluid is always positively shear dilatant.

For two-dimensional systems mode-coupling theory predicts [4–7] negative shear dilatancy in a finite range of shear rates $\gamma \geqslant 0$, about equilibrium. In early two-dimensional simulations for small systems ($N < 100$), negative dilatancy had actually been observed [43]. The mode-coupling constitutive relation $p(\gamma) \sim \gamma \ln \gamma$ was consistent with all the low-shear rate data. In 1984, Evans and Morriss [44], however, found in much larger two-dimensional simulations ($N \sim 3584$), that flow instabilities "screen out" the negative dilatancy region and the corresponding mode-coupling logarithmic divergence of the shear viscosity.

Another prediction from thermodynamic fluctuation theory is that if the leading term in the shear dilatancy constitutive relation is $p(\gamma) = p(0) + p_1(T, V)\gamma^m$, then the shear dilatancy exponent m must be strictly less than 2 [45]. Because of the relationship between dimensionality and the mode-coupling exponents, one would have expected that in four dimensions the viscosity exponent should be 1 and the dilatancy exponent exactly 2! (see Table I). In 1984, we [46] carried out simulations in a four-dimensional fluid. The mode-coupling exponent for viscosity was verified but the observed dilatancy exponent was 1, consistent with thermodynamic constraints.

We believe that it is quite possible that the high-shear rate phase change observed by Erpenbeck [31] is also consistent with thermodynamic predictions. Indeed the instability of normal fluid flow at high shear rates had already been predicted from thermodynamic considerations by Hanley and Evans in 1982 [40] What is needed now is accurate simulation data to show that the onset of the Erpenbeck phase corresponds to the breakdown of thermodynamic stability criteria for normal fluid shear.

5. FUTURE

Attempts to predict the future course of research are usually doomed to failure. Sometimes, however, such attempts do serve the useful purpose of highlighting important unresolved problems in a given field. We attempt to make a few such comments here.

We have arrived at the stage where, particularly for studies in the linear regime close to equilibrium, we have an efficient armory of NEMD simulation techniques for studying heat, mass, and momentum flows in dense fluids. For the special case of shear flow, our algorithms are known to be correct arbitrarily far from equilibrium. The range of interesting problems that can be tackled with these methods is limited only by access to computer time. Studies have already begun into turbulence. With improvements in computer hardware we can now make a start at simulating molecularly complex fluids which are known to be non-Newtonian from experimental studies.

From a theoretical point of view, our greatest need is for a *usable* form of nonlinear response theory. Do steady-state time correlation functions have any useful hydrodynamic meaning far from equilibrium? In view of the usefulness of Green–Kubo relations for devising linear NEMD algorithms, are there any corresponding relations for transport far from equilibrium? In this context the requirement for usefulness is very important. There is little advantage in knowing a formally exact expression for the nonlinear nonequilibrium distribution function if it is so intractible that no computational test of its validity can be devised.

Although much effort has recently gone into trying to understand "enhanced long-time tail behavior," there still is no concensus among theoreticians regarding their explanation. Keyes' ideas seem to derive the greatest support from simulation data. However, Keyes' theory is completely phenomenological. Using statistical mechanical theory, is it possible to derive Keyes' scaling relations microscopically? If the answer is yes, the problem of "enhanced tails" is fundamentally solved.

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