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Non-Newtonian Molecular Dynamics and Thermophysical Properties[1]

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The main theme of the paper is to review computer simulation as a tool to study mechanisms in fluids and to understand better fluid behavior. The relationship between molecular dynamics and thermophysical properties of fluids is reviewed very briefly. The standard simulation algorithms that are available are listed. We emphasize, however, the importance of the recent molecular dynamics techniques that incorporate non-Newtonian equations of motion. Two topics are introduced as examples. First, the evidence of a transient solid-like structure observed from simulations of a dense model two-dimensional liquid is reported: we speculate that the transient structure influences the density dependence of many thermophysical properties of the real liquid. Second, a discussion of the structure factor of a system under shear, and its relation to the properties of the fluid, is given.

KEY WORDS: fluid properties; liquids; molecular dynamics; non-Newtonian behavior; non-Newtonian equations of motion; structure factor; transient fluid structure; two-dimensional model liquid.

1. INTRODUCTION

Molecular dynamics is the most common variant of computer simulation, and one could argue that computer simulation is the single most important procedure in condensed matter theory introduced since the turn of the century. Simulation is completely integrated with thermodynamics and

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statistical mechanics. Many basic techniques are standard and unlikely to change in the future. In fact, it is not even necessary to have a background in computing to use its tools. Nevertheless, the potential of simulation is only beginning to be fully realized. New results are published almost every day. We discuss here a very recent versatile molecular dynamics that incorporates non-Newtonian equations of motion for a system.

The paper is organized by first commenting briefly on the principles of molecular dynamics. A list of references for the techniques and algorithms available is presented. The basic concepts of the new molecular dynamics method are then outlined. Two applications from our own work are discussed to illustrate the power of simulation to understand better liquid behavior and to show how simulation contributes to the prediction of thermophysical properties.

As an introductory aside, we would like to remark that property data are often treated in isolation without any real feel for what they represent. Hence it is important to recall that properties are the quantitative measure of how a system responds to a disturbance; data are characteristic of a phenomenon. We feel, therefore, that one needs to understand the phenomenon as best one can to get a better representation of the data. Computer simulation is invaluable in this context. We also assume that the principle goal of theoretical fluid property work is to develop predictive procedures and that it is taken for granted that these procedures should be as soundly based on statistical mechanics as possible.

2. BASICS OF MOLECULAR DYNAMICS

The concepts and techniques of molecular dynamics (MD) are well documented. There are two sources that are particularly useful: a very recent text, *Computer Simulation of Liquids*, by Allen and Tildesley [1], and the article on non-Newtonian molecular dynamics by Evans and Morriss [2]. These references include practical discussions on programming and list many computer codes. The manual of Haile [3] is also very helpful. An important source of current information on algorithms and programming is the *Daresbury Laboratory Information Quarterly* [4]. The symposia proceedings of Ref. 5 contain a typical cross section of current work on applications of simulation to applied statistical mechanics and thermodynamics. The *International Journal of Thermophysics* is a particularly good source for articles with this bias, especially the volumes reporting on the 9th Symposium on Thermophysical Properties [6] and the forthcoming issues for the 10th Symposium.

For more formal discussions on the state-of-the-art of simulation, we recommend the conference proceedings published as Ref. 7. The inter-relation of computer simulation with fundamental statistical mechanics, especially with regard to non-Newtonian molecular dynamics, is discussed in the lecture notes of Hoover [8] and in the forthcoming book by Evans and Morriss [9].

2.1. Conventional Molecular Dynamics: The Microcanonical Ensemble

The basis of a molecular dynamics simulation of a fluid is the solution of Newton's equation of motion. At a given density, ρ, N molecules (typically 100–200) of mass m are placed in a box, the unit cell, of volume V such that the density $\rho = N/V$ and $V = L^3$, where L is the box length. The molecules are given initial positions $\mathbf{r}_i(0)$, and velocities, $\dot{\mathbf{r}}_i(0)$, with $i = 1, N$. The usual practice is to reduce all variables by a length, energy, and mass parameter and set the parameters equal to one. The time evolution of the system follows from a solution of Newton's equations:

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m \qquad \text{and} \qquad \dot{\mathbf{p}}_i = \mathbf{F}_i \tag{1}$$

where $\mathbf{p}_i$ is the peculiar momentum of particle i and $\mathbf{F}_i = -\sum \partial\phi_{ij}/\partial\mathbf{r}_{ij}$, with ϕ_{ij} the intermolecular pair potential energy and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The equations are solved numerically using a time step or increment, Δt. The properties of the fluid are the appropriate statistical averages taken over several thousand time steps. The kinetic temperature is $T = (1/3N)\sum m\dot{r}_i^2$, for example. The fact that we have to work with a small a number of particles (compared with Avogadro's number of 10^{23}) is compensated for by incorporating periodic boundaries, i.e., by surrounding the unit cell with an infinite array of its periodic images. The potential energy of particle i is evaluated by considering the shortest distance between particle i and particle j, whether j is in the unit cell or is an image. Further, should a particle leave the cell in the course of time, it is replaced by its image from a neighboring cell.

The main requirements of MD are as follows.

(i) The pair potential characteristic of the particles is given; if the particles are molecules with structure, the atom–atom potential and the constraints of the model molecule (i.e., rigid diatomic, etc.) are given.

(ii) Usually, but not necessarily, the total potential, Φ, is taken as the sum of the potential from all particle pairs.

(iii) The particles in the box are assumed to represent the system as a whole unless specific steps are taken to ensure otherwise. Caution is needed if the range of the pair potential is of the order of L.

2.2. Non-Newtonian Molecular Dynamics

The basis of conventional MD is standard; programming details and tricks are described in Refs. 1 and 3, for example. Conventional MD is not ideal, however. Solving Newton's equations of motion restricts the simulation to the (N, V, E) microcanonical ensemble and this ensemble is not convenient in practice since a more practical set of variables, such as the temperature and/or pressure, is often preferred. This limitation was addressed by Evans [2] and by Hoover [8] and their co-workers. Evans and Hoover proposed a broader simulation technique based on general equations of motion of which Newton's are a special case.

Consider an N-particle system subject to a constraint that can be written in the form,

$$g(\mathbf{r}, \dot{\mathbf{r}}, t) = 0 \tag{2}$$

where $\mathbf{r}$ and $\mathbf{r}$ are $3N$-dimensional vectors. In general, g depends on the position and velocity of the particles and on time. Differentiation of Eq. (2) with respect to time gives the differential form for the constraint equation,

$$\mathbf{n}(\mathbf{r}, \dot{\mathbf{r}}, t) \cdot \ddot{\mathbf{r}} = \mathbf{s}(\mathbf{r}, \dot{\mathbf{r}}, t) \tag{3}$$

where $\mathbf{n}$ and s are also functions of position velocity and time in general. The constraint satisfying equation of motion can be written as

$$\dot{\mathbf{p}} = \mathbf{F} - \lambda\mathbf{n} \tag{4}$$

where $\mathbf{F}$ is the unconstrained (Newtonian) force and $\lambda\mathbf{n}$ is the force of constraint. The direction of the constraint force is determined from the condition that its magnitude is a minimum. Substitution of Eq. (4) into Eq. (3) yields for the multiplier, λ,

$$\lambda = [(\mathbf{n} \cdot \mathbf{F}) - s]/n^2 \tag{5}$$

Example: The Isokinetic Ensemble. Suppose the constraint function g is

$$\sum (1/2)\, m\dot{r}_i^2 - (3/2)\, Nk_{\mathrm{B}} T = 0. \tag{6}$$

This constraint will fix the equipartition estimate for the temperature. Differentiating Eq. (6) so that it is in the form of Eq. (3), we get

$$\sum \mathbf{p}_i \cdot \dot{\mathbf{p}}_i = 0. \tag{7}$$

Hence the equation of motion for particle i is

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \lambda \mathbf{p}_i \tag{8}$$

with λ given by

$$\lambda = \sum \mathbf{F}_i \cdot \mathbf{p}_i \Big/ \sum p_i^2 \tag{9}$$

One sees that only a trivial modification to a conventional MD program is required to fix the "kinetic temperature."

It is straightforward to show that the ensemble generated by these equations of motion is canonical at equilibrium for the configurational degrees of freedom $[e^{-\beta\Phi}]$ and microcanonical for the kinetic degrees of freedom $[\delta(K-3NkT/2)]$. The ensemble is thus halfway between a canonical and a microcanonical ensemble. (Nose and Hoover have, however, proposed slightly more complex equations of motion which generate the true canonical ensemble [8].)

As an aside, we remark that this new approach to molecular dynamics has often been misunderstood. It is important to remember that, while the motion of particles obey Newton's equations in principle, one can solve these equations only for an *isolated* system, and no macroscopic systems are ever totally isolated. The isokinetic equations of motion provide a dynamics which correctly predicts the equilibrium macroscopic properties of the isokinetic ensemble. In the thermodynamic limit, thermophysical properties are insensitive to the precise details of the microscopic particle trajectories. Many sets of equations of motion can, in principle, produce identical and correct thermodynamic averages. We should use the simplest and most convenient dynamics. These new dynamical systems are simply the dynamical generators of Gibbs' various equilibrium ensembles. It has also been proved that in the thermodynamic limit, isokinetic dynamics correctly predicts equilibrium time correlation functions and therefore *linear* transport coefficients.

Example: Nonequilibrium Molecular Dynamics (NEMD). A most attractive feature of non-Newtonian molecular dynamics is that one can simulate the behavior of a system out of equilibrium. Let us consider an isokinetic system subject to planar Couette flow. The shear rate γ, defined as $\partial u_x/\partial y$, where $\mathbf{u}$ is the streaming velocity, is imposed on the system by means of time varying displaced periodic boundaries. Should a particle leave the unit cell through a face parallel to the x-axis, it is replaced by its reentrant image displaced in the x-coordinate by $\pm\gamma L\,\Delta t\,\mathbf{n}_x$, where $\mathbf{n}_x$ is a unit vector in the x-direction. Its velocity is shifted by $\pm\gamma L\mathbf{n}_x$.

The thermostated equations of motion for the system using the constraint Eq. (6) are

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m + \mathbf{n}_x \gamma y_i, \qquad \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{n}_x \gamma p_{yi} - \lambda \mathbf{p}_i \tag{10}$$

and λ is the thermostating multiplier given by

$$\lambda = \frac{\sum (\mathbf{p}_i \cdot \mathbf{F}_i - \gamma p_{xi} p_{yi})}{\sum \mathbf{p}_i^2} \tag{11}$$

Example: The Rigid Diatomic Molecule. The idea of writing a convenient equation of motion with constraints is quite general and can be applied in principle to any system provided the constraint can be cast in the form of Eq. (2). For a diatomic fluid of rigid molecules, for example, if $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ is the bond vector, we can write

$$\mathbf{r}_{12} \cdot \ddot{\mathbf{r}}_{12} + \dot{\mathbf{r}}_{12}^2 = 0 \tag{12}$$

The constrained equations of motion for sites 1 and 2 are thus

$$\dot{\mathbf{p}}_1 = \mathbf{F}_1 + \lambda \mathbf{r}_{12}, \qquad \dot{\mathbf{p}}_2 = \mathbf{F}_2 - \lambda \mathbf{r}_{12} \tag{13}$$

whence

$$\lambda = [\mathbf{F}_{12} \cdot \mathbf{r}_{12} + \dot{\mathbf{r}}_{12}^2]/2r_{12}^2 \tag{14}$$

where $\mathbf{F}_{12} = \mathbf{F}_2 - \mathbf{F}_1$.

The three examples demonstrate the versatility of the approach. Combinations of constraint conditions are, of course, possible; for instance, one could write the equations of motion for a system of rigid diatomic molecules undergoing shear at constant temperature from the equations we have given here. We refer to Ref. 2 for details and for discussions of many other applications.

3. THE BEHAVIOR OF LIQUIDS

Our understanding of fluid behavior has been richly enhanced by computer simulation. A simulation is *unambiguous*; the results reflect exactly the effects of an assumption imposed on the model liquid. Further, we have exact control of the "experimental" variables. We can thus probe a system on a time or length scale that would be difficult or impossible to replicate in the laboratory.

The early simulations of the hard sphere fluid—simulations of the equilibrium behavior [10] and simulations of the self-diffusion coefficient [11], in particular—revitalized the theory of liquids. For example, the equilibrium results demonstrated that a fluid could freeze without Van der Waals attraction. They emphasized the dominant role played by particle size (the radial distribution function of a dense hard sphere liquid is very similar to that of real simple liquids). The numerical results for the hard sphere liquid meant that powerful perturbation theories of liquids could be used as practical tools [12]. In the context of thermophysical properties, the last two consequences are the basis directly or indirectly for nearly every prediction procedure. The self-diffusion studies demonstrated the importance of long-range phenomena in a liquid and were the impetus for a complete reevaluation of classical kinetic theory and nonequilibrium statistical mechanics.

We present here two recent examples of how a molecular dynamics simulation increases our understanding of fluids, and the relevance of the results to the prediction of thermophysical properties is pointed out. Both examples involve calculating the structure factor, $S(\mathbf{k})$, where $\mathbf{k}$ is the momentum transfer, of the two-dimensional soft disk liquid whose particles interact with the $1/r^{12}$ potential. The simulations were based on the constrained equation of motion algorithms outlined in Section 2. There is little loss of generality in looking at the structure factor of a fluid in two, as opposed to three, dimensions; the results are more easily realized and are more straightforward to interpret. The simple potential model is also not restrictive because, as remarked, the structure of the liquid is dominated by the fact that the particles have size.

3.1. Transient Structure in a Dense Liquid

The first example addresses the experimental observation that several thermophysical properties are very strong functions of density, especially at densities exceeding about $2.5\rho_c$ (or exceeding two-thirds of the freezing density), where ρ_c is the critical density. Figure 1 shows the density dependence of the velocity of sound and the viscosity; Fig. 1a illustrates the velocity of sound of ethane [13], and Fig. 1b the viscosity of propane [14]. The behavior of both properties is typical for all relatively simple fluids. The density variation for the viscosity is particularly dramatic. In general, thermophysical properties can be predicted from conventional corresponding states and the statistical mechanical theories of liquids if the density is less than about twice critical; above that density, the conventional theories of liquids tend to break down. Alternatively, some authors base predictive procedures on the behavior of the solid or the very dense liquid. In these cases the procedures do not extrapolate well to the lower densities. The problem is to account correctly for the marked density behavior.

We reported in Ref. 15 a study of transient local order in the two-dimensional soft disk fluid. The objective was to evaluate $S(\mathbf{k})$ as a function of time and of position in the system. Simulations were carried out for 896 particles at a reduced temperature of 1 and for reduced densities in the range $0.3 \leqslant \rho \leqslant 0.98$ and for one density of 1.05 in the solid (the freezing density is 0.986). The simulation technique made use of the isokinetic ensemble equations described in Section 2.2 [2]. To evaluate $S(\mathbf{k})$ we extracted the positions, $\mathbf{r}_i$, of the particles from the simulation run at an arbitrary time. These positions were then represented as transparent dots on black photographic film. We then regarded the film as a scattering medium. The structure factor was obtained by the direct measurement of the diffraction pattern from the film when light from a He/Ne laser was passed through it. Composite plots were prepared that consisted of 36 sets taken at random times from the simulation.

The procedure was repeated for a system of 3584 particles: structure factors were extracted by viewing the sample as a chole and by stopping down the light aperture to look at smaller segments of about 800 particles.

Averages of the structure factors for the 896-particle system are shown in Fig. 2. Figure 2a displays the hexagonal crystalline pattern of the solid at $\rho = 1.05$, Fig. 2b depicts the typical radially symmetric pattern of the dense liquid at $\rho = 0.95$, and Fig. 2c shows the diffuse pattern of the moderately dense liquid at $\rho = 0.3$. Contrast Fig. 2b, however, with some

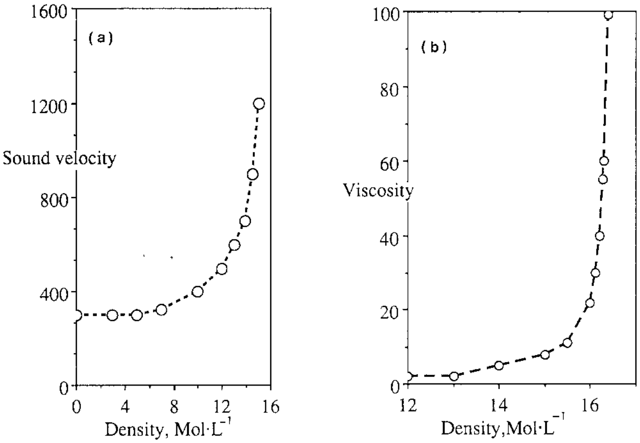

Fig. 1. (a) The density variation of the velocity of sound ($\mathrm{m \cdot s^{-1}}$) of ethane at room temperature [13]. The critical density of ethane is $6.7\ \mathrm{mol \cdot L^{-1}}$. (b) The density behavior of the viscosity ($10^2\ \mathrm{Pa \cdot s}$) of propane at saturation [14]. The critical density of propane is $5.1\ \mathrm{mol \cdot L^{-1}}$.

snapshots of $S(\mathbf{k})$ from individual configurations at $\rho = 0.95$, shown in Fig. 3. Figure 3a shows the pattern expected of the liquid, but Fig. 3b, taken from the simulation 50 time steps later, indicates anisotropic features typical of the microstructure of the solid. In particular, the second diffuse ring in Fig. 3b appears hexagonal, while there are six bright spots in the inner ring. This hexagonal structure was clearly seen in approximately half the snapshots, and of course, the orientation of the hexagon varied.

The structure factor of the 3584 particle liquid at $\rho = 0.9238$ is given in Fig. 4. Figure 4a is $S(\mathbf{k})$ for the complete sample, i.e., obtained by

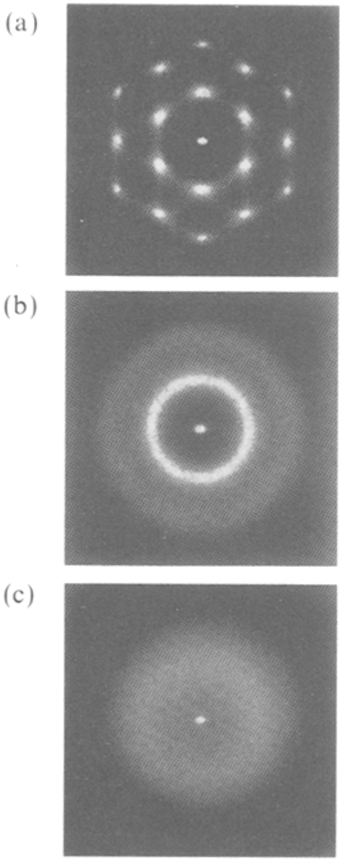

Fig. 2. The average structure factors for an 896-particle soft disk liquid at three densities: (a) the solid at $\rho = 1.05$; (b) the dense liquid at $\rho = 0.95$; (c) the liquid at $\rho = 0.3$.

exposing the film with all the particles to the laser beam, while $S(\mathbf{k})$ in Figs. 4b and c were obtained from segments of the sample of about 800 particles. Again, we see evidence of hexagonal order but recorded as a function of location within the system at a given time rather than of time as before.

Order Parameter. The degree of hexagonal order was correlated as a function of density in terms of an order parameter, ζ, defined as $\langle \cos 6\theta \rangle$, where θ is the orientation angle between a particle and its neighbor found in a ring thickness *dr*, distance *r* away. The natural log of ζ is plotted versus density in Fig. 5. ζ varies from a value of 0.5 for the solid to essentially zero at about 0.7 of the freezing density.

The analogy between the behavior of the order parameter in Fig. 5 and the density behavior of the thermophysical properties in Fig. 1 and its

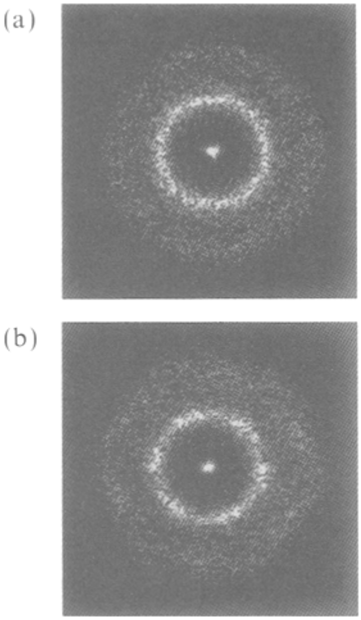

Fig. 3. The structure factor for the liquid at $\rho = 0.95$ evaluated by light scattering from the simulation at two random times: (a) displaying a circular pattern; (b) with evidence of the solid-like hexagonal pattern, especially in the second band.

relevance to prediction procedures is very obvious. If the degree of hexagonal order at a given density in a *model* fluid could be explained and predicted, then we would have a better insight as to why the density dependence of most *real fluid* properties is so strong. From the viewpoint of predicting the properties, the information learned could be invaluable.

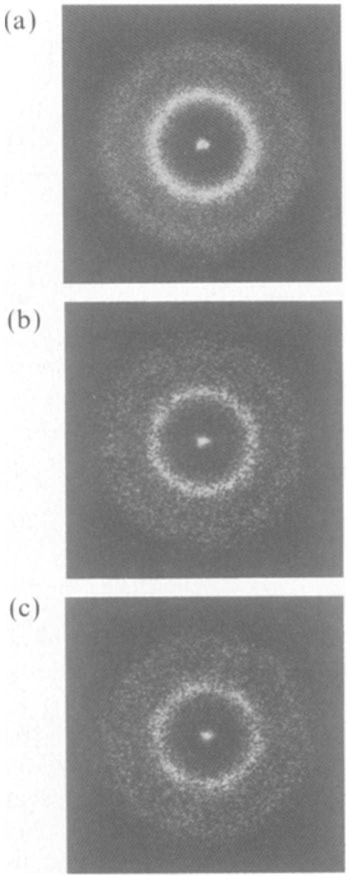

Fig. 4. $S(\mathbf{k})$ for the 3584-particle liquid at a density of 0.9238. The $S(\mathbf{k})$ (a) from exposure of the whole area of sample and (b, c) from different subsections of the area, each subsection containing about 800 particles. Note the hexagonal appearance in c.

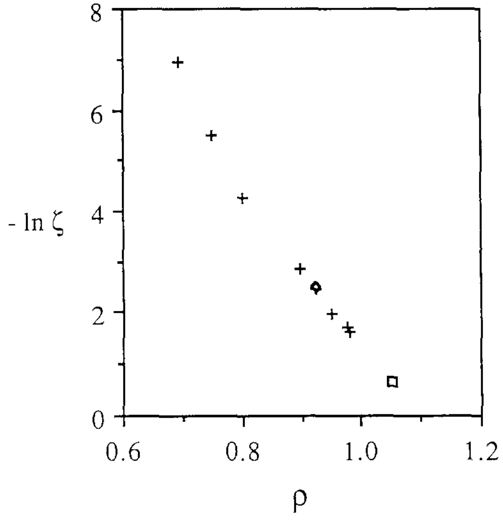

Fig. 5. Plot of the order parameter versus density. The crosses are from the 896 system, the circle is from the 3584 system, and the square is the point from the solid.

3.2. Non-Newtonian Behavior

For our second example we discuss the contribution of nonequilibrium molecular dynamics to understand better the non-Newtonian or rheological behavior of liquids.

Background. There is a traditional and arbitrary segregation between so-called "simple" and so-called "complex" liquids. Simple liquids are typified by argon, air, or gasoline, while complex liquids are bread dough, polymeric solutions, paint, and the like. A characteristic of the latter group is an exotic response under shear, apparently quite different from the corresponding response of simple liquids [16]. Shampoo does not flow in the same way as water, for example. Complex fluids are non-Newtonian (i.e., they do not obey Newton's law of viscous flow). One form of non-Newtonian behaviour is a shear rate dependent viscosity, e.g.,

$$P_{xy} = -\eta(\gamma)\gamma \tag{15}$$

where η is the shear viscosity, γ is the shear rate, and P_{xy} is the xy component of the pressure tensor, **P**. Other forms of non-Newtonian behaviour include time- or, equivalently, frequency-dependent viscosity (namely, viscoelasticity) and normal pressure differences (namely, Weissenberg effects) that arise because the diagonal elements of **P** are unequal, i.e.,

$$P_{xx} \neq P_{yy} \neq P_{zz} \tag{16}$$

Computer simulation demonstrates that the separation between simple and complex fluids is indeed arbitrary because simulation results show that a simple fluid has non-Newtonian characteristics. Figure 6 displays the viscosity of a WCA (Weeks, Chandler, Anderson) fluid undergoing Couette flow evaluated by NEMD using the thermostating equations of motion, Eqs. (10) and (11). The viscosity is a linear function of $\gamma^{1/2}$. The result in Fig. 6 is typical of a spherical model liquid. The simulation of non-Newtonian behavior of simple liquids and the consequences for the study of rheology in general have been discussed at length elsewhere [2, 7, 8, 17, 18]. The principle conclusion of interest here is that one cannot distinguish between conventional Newtonian and non-Newtonian liquids on the basis of molecular structure alone. In fact, the NEMD data indicate that a Newtonian liquid is only a convenient abstraction, similar in spirit to the dilute gas. Contrary to widespread belief, therefore, non-Newtonian characteristics are not due solely to shear induced changes in *intra-*

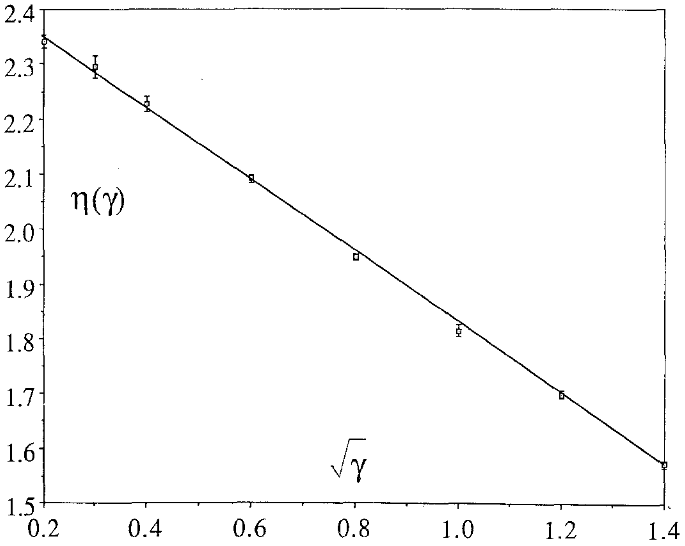

Fig. 6. Plot of the viscosity versus shear rate of a Weeks Chandler Anderson (WCA) liquid at its triple point. The error bars at low γ are quite large. The fact that this simple fluid is thus non-Newtonian is discussed in the text.

molecular structure—such as the uncoiling of a polymer. Shear-induced distortions in the *inter*molecular microstructure must be of paramount importance. We, therefore, thought it would be worthwhile to examine the structure of a sheared liquid via the structure factor, $S(\mathbf{k})$.

The Structure Factor of a Sheared Two-Dimensional Fluid. We have discussed the simulation of the structure factor of model liquids in several papers and our results are summarized in Refs. 19 and 20. We illustrate the essence of the calculations here for the two-dimensional soft disk fluid close to freezing [21].

The structure factor was evaluated by the method outlined in Section 3.1 with a shear imposed on the system: 896 soft disks interacting with the r^{-12} potential at a temperature of 1 and a density of 0.9238 were subjected to shear rates in the range $0.1 \leqslant \gamma \leqslant 10$. We evaluated $S(\mathbf{k})$ directly as the average diffraction pattern obtained from photographs of the particle positions taken at random intervals from the simulation. The structure factor for the system at a shear rate $\gamma = 1.0$ is shown in Fig. 7. Reference 21 gives details and the results for the other values of γ. Compare Fig. 7 with Fig. 2. The main difference is the distortion of the diffuse rings from a circle to an approximate ellipse with a major axis at about $3\pi/4$.

The interpretation of the distorted structure factor is perhaps easier to explain in terms of the pair correlation function, $g(\mathbf{r}, \gamma)$, which is the

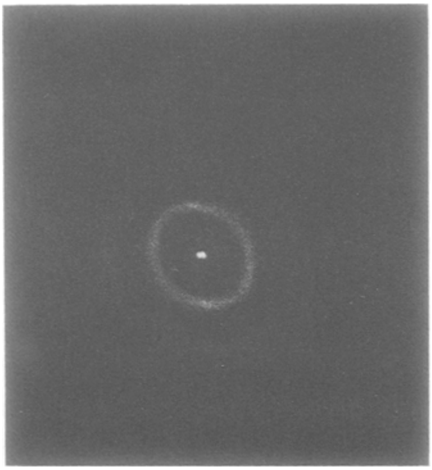

Fig. 7. The structure factor of a two-dimensional soft disk liquid at $\rho = 0.9238$ subjected to a shear of $\gamma = 1.0$. Note the elliptical shape of the diffuse bands.

Fourier transform of $S(\mathbf{k})$. The correlation function can be expanded by a Fourier series in polar coordinates:

$$\begin{aligned} g(\mathbf{r}, \gamma) &= g(r, \theta, \gamma) \\ &= g_s(r, \gamma) + \sum \left[g_0^{(n)}(r, \gamma) \sin n\theta + g_1^{(n)}(r, \gamma) \cos n\theta \right] \end{aligned} \tag{17}$$

where (excluding the γ dependence from the subsequent notation)

$$g_s(r) = (1/2\pi) \int d\theta \; g(r, \theta) \tag{18}$$

and

$$g_0^{(n)}(r) = (1/\pi) \int d\theta \; g(r, \theta) \sin n\theta \tag{19}$$

$$g_1^{(n)}(r) = (1/\pi) \int d\theta \; g(r, \theta) \cos n\theta \tag{20}$$

Figure 8 shows the schematic relationship between the pair correlation function and the distorted structure. At equilibrium $g(\mathbf{r}, \gamma) \Rightarrow g_{\mathrm{eq}}(r)$, the

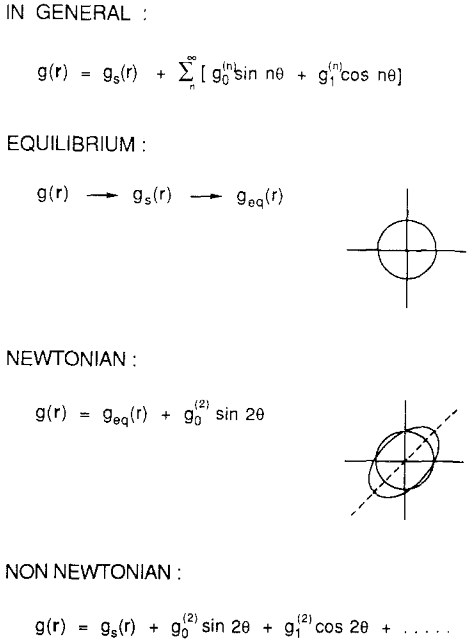

Fig. 8. Schematic equations and diagrams illustrating the relation between the pair correlation function and the distorted microstructure of a fluid under shear.

radial distribution function, and an intensity plot of the Fourier transform $S(\mathbf{k})$ is radially symmetric. For a Newtonian liquid, g_s of Eq. (17) is $g_{eq}(r)$ and the only other nonvanishing term in the expansion (17) is $g_0^{(2)}(r, \gamma)$ $\sin 2\theta$. The structure factor is an ellipse with the major axis at $3\pi/4$. In the general case, (i.e., for a non-Newtonian fluid), all the coefficients are nonzero and the major axis of the ellipse moves off $3\pi/4$.

The point made at the end of Section 3.1 is equally valid here. If we can understand the distortion of the microstructure of the model liquid, and if the expansion coefficients can be predicted, then one has made considerable progress in understanding the rheological behavior of real liquids. It turns out that we can indeed predict the coefficients to order $n=4$ quite well, see Ref. 22.

As is well known, the pair correlation function and the structure factor are measures of the thermophysical properties. The configurational parts of all thermophysical properties can be written as functionals of these distribution functions. This implies that the thermodynamic properties of a sheared fluid are γ dependent. The thermodynamic properties of the fluid are given by the appropriate integrals of $g_s(r, \gamma)$. The shear viscosity coefficient and coefficients for the normal pressure differences are given by the appropriate integrals of $g_i^{(2)}(r, \gamma)$, $i=0, 1$.

4. SUMMARY AND CONCLUSIONS

The two examples indicate how our understanding of the behavior of liquids is enhanced by studying a model fluid via molecular dynamics. Our objective has been to outline the contribution of MD to the theory of liquids in general and its role in predicting thermophysical properties in particular. The power and versatility of the simulation approach, however, are further illustrated by noting what has *not* been discussed in this short review.

First, we have considered only molecular dynamics and thus have not covered other simulation techniques such as the Monte Carlo (see Ref. 1 for a description of these methods). But we should point out that there is often no advantage in using Monte Carlo since the thermodynamic constraint techniques are available. All of Gibbs ensembles are now amenable to MD. (The single exception is the grand canonical ensemble.)

Second, we have barely mentioned the most common use of simulation: MD is an essential tool for unambiguously testing a statistical mechanical theory. MD performs essentially exact statistical mechanical calculations for a precisely defined model system. In assessing prediction procedures by comparison with experimental data, one cannot always be sure whether failures arise because of an approximate intermolecular potential function or because the statistical mechanical assumptions are at fault. The experimental data themselves may also be suspect. The problem is especially relevant today because of the interest in predictive procedures for the properties of mixtures. There is a substantial body of work on the applied statistical mechanics of mixtures and the proper choice of mixing rules: the prediction of the phase behavior of mixtures is especially sensitive to the scaling procedures and the mixing assumptions. Many authors are discussing the problem of extending corresponding states to include, for example, polar species. It is obvious from the literature that these lines of study would not exist without the backup of simulation [23].

Third, we have not mentioned the merits of computer "data" with respect to real experimental data. In spite of the difficulties in accurately determining intermolecular potential functions, there are a number of circumstances where computer simulations using accurate potentials provide the only reliable "experimental" information. Two well-known examples are geophysical fluid dynamics, where thermophysical properties are required for materials under extreme conditions of temperature and pressure, and protein and membrane dynamics, where simulation often provides the *only* source of information concerning molecular conformation and unfolding. (The interpretation of real experimental data is often so model dependent that it is completely unreliable.)

Finally, this paper has not discussed the simulation of processes, such as fluid flow around a plate, the Weissenberg effect, flows in nozzles, studies in turbulence, and similar phenomena.

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