NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATION OF DENSE FLUID METHANE

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We present a non-equilibrium molecular dynamics simulation of 125 methane molecules using a variant of the isokinetic “sslod” algorithm. The shear viscosity, pressure and internal energy of methane in a dense, supercritical fluid state (temperature 285.7 K and mass density 0.288 g/cm$^3$) are calculated and the viscosity compared with experiment, with excellent agreement: the predicted shear viscosity is within 1% of the experimental value, improving on the result obtained for this same system by Evans (~10% agreement). We attribute the improvement to the improved non-equilibrium algorithm used. The model for the intermolecular potential is a site-site exponential, with only two-body interactions being considered.

1. Introduction

In recent years, the non-equilibrium molecular dynamics (NEMD) technique has developed into a powerful tool for the study of transport properties of both simple and molecular fluids [1-3]. The most promising recent developments include the derivation of synthetic techniques for calculating such properties as the shear viscosity, thermal conductivity and self-diffusion and the use of Gauss’ principle of least constraint into a tool for constraining simulations in physically meaningful ways (yielding, for example, isokinetic and/or isobaric ensemble simulations [2,4,5]). Finally, the validity of these and other NEMD techniques has been established in recent years through linear response theory [6,7].

Among the many NEMD methods which have been developed for calculating the shear viscosity — reviewed in section 3 of ref. [2] — the most efficient technique appears to be the “sslod” algorithm, a synthetic non-equilibrium algorithm which sets up a steady state planar Couette flow with the two plates moving in opposite x directions located at $y = \pm \infty$ so that the streaming velocity has a non-zero component in the x direction, $u_x$, which satisfies

$$\frac{du_x}{dy} = \gamma.$$  

In this equation, $\gamma$ is the constant strain rate. In the sslod algorithm simulation, as with many other NEMD algorithms for shear viscosity which employ planar Couette flow, the usual periodic boundary conditions prevail in the x and z directions; in the y direction, however, the periodic image cells move in the positive and negative x directions according to the strain rate $\gamma$ (the so-called “sliding brick” Lees-Edwards boundary conditions [9]). Consequently, a molecule leaving the top (bottom) of the simulation cell re-enters at the bottom (top) shifted to the left (right) by an amount $\gamma L t$ (where $L$ is the length of the side of the cubic simulation cell and $t$ is time) and with the x component of its velocity reduced (increased) by an amount $\gamma L$. An algorithm for this imaging procedure is given by Evans and Morriss [2]. The isokinetic sslod equations of motion for a monatomic fluid are given by Evans and Morriss [2] as

$$\frac{dr_j}{dt} = \frac{p_j}{m} + r_j \cdot \nabla u, \quad (2a)$$

$$\frac{dp_i}{dt} = F_i - p_i \cdot \nabla u - \lambda p_i, \quad (2b)$$

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3 The earliest reference to the sslod algorithm is attributed to Hoover and Ladd [8] by Evans and Morriss [6].
where $V$ is the gradient operator, $r_i$ is the position of the center of mass of molecule $i$, $p_i$ is the translational momentum of molecule $i$, $F_i$ is the force on the center of mass of molecule $i$ and $u$ is the streaming velocity (which for the planar Couette flow described by eq. (1) is given by $u = (\gamma y, 0, 0)$). The parameter $\lambda$ is given by

$$
\lambda = \sum_{i=1}^{N} (p_i \cdot F_i - p_i p_i \cdot V u) / \sum_{i=1}^{N} p_i^2 ,
$$

(3)

where $\cdot$ indicates the full contraction of two second-order tensors and $N$ is the number of molecules in the simulation cell. The formula of $\lambda$ is dictated by requiring that the temperature $T$ remains fixed, which is equivalent to demanding that $\sum_{i=1}^{N} p_i^2$ remain a constant of the motion. Thus the isokinetic slab equations maintain a steady state planar Couette flow at constant temperature.

For a molecular fluid, two modifications of these equations of motion are necessary. First, the rotational motion of the molecules must be included and second, the constant temperature constraint may profitably be modified since by the classical energy equipartition theorem the temperature is also related to the angular momentum of the molecules (as well as the linear momentum). We begin by addressing the first issue. Using the quaternion representation for the rotational motion [10,11], the usual rotational equations of motion for molecule $i$ are given by

$$
\frac{dL_i}{dt} = T_i,
$$

(4)

$$
L_i^p = A_i L_i ,
$$

(5)

$$
\omega_{i\beta}^p = \frac{L_i^p}{I_{i\beta}}, \quad \beta = x, y, z,
$$

(6)

$$
\frac{d}{dt} \begin{bmatrix} q_{11} \\ q_{12} \\ q_{13} \\ q_{14} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -q_{13} & -q_{14} & q_{12} & q_{11} \\ q_{14} & -q_{13} & -q_{11} & q_{12} \\ q_{11} & q_{12} & -q_{14} & -q_{13} \\ -q_{12} & q_{11} & q_{13} & -q_{14} \end{bmatrix} \begin{bmatrix} \omega_{i\alpha}^p \\ \omega_{i\beta}^p \\ \omega_{i\gamma}^p \\ 0 \end{bmatrix} ,
$$

(7)

where $L_i$ is the angular momentum of molecule $i$ and $T_i$ is the torque on molecule $i$ in the laboratory frame, $L_i^p$ and $\omega_{i\beta}^p$ are respectively the angular momentum and angular velocities of molecule $i$ in its principal axis frame, $A_i$ is the rotation matrix which transforms vectors from the laboratory to principal axis frame of molecule $i$, $I_{i\beta}$ is the principal axis moment of inertia of each molecule and the $q_{i\alpha}$, $\alpha = 1, 2, 3, 4$ are the quaternion parameters related to the Euler angles describing the orientation of molecule $i$ in space. As this formalism is described elsewhere in detail [10,11], we do not consider it any further here.

We now turn our attention to the second issue—that is, the method for constraining the kinetic energy (and hence the temperature) to be a constant of the motion. For a fluid containing $N$ non-linear molecules such as methane this constant temperature (isokinetic) constraint demands that

$$
\frac{1}{2m} \sum_{i=1}^{N} p_i^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{\beta=1}^{3} I_{i\beta} (\omega_{i\beta}^p)^2 - 3NkT = 0 ,
$$

(8)

where $k$ is Boltzmann's constant and $T$ is the absolute temperature. The first term represents the translational kinetic energy and the second represents the rotational kinetic energy. By applying Gauss' principle of least constraint to the equations of motion (2) and (4)-(7), it can be shown [12] that in satisfying isokinetic constraint (8) we obtain the following, complete set of equations of motion:

$$
\frac{dr_i}{dt} = p_i/m + r_i \cdot Vu ,
$$

(9a)

$$
\frac{dp_i}{dt} = F_i - p_i \cdot Vu - \lambda p_i ,
$$

(9b)

$$
\frac{dL_i}{dt} = T_i - \lambda T_i ,
$$

(10a)

$$
L_i^p = A_i L_i ,
$$

(10b)

$$
\omega_{i\beta}^p = \frac{L_i^p}{I_{i\beta}}, \quad \beta = x, y, z,
$$

(10c)

$$
\frac{d}{dt} \begin{bmatrix} q_{11} \\ q_{12} \\ q_{13} \\ q_{14} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -q_{13} & -q_{14} & q_{12} & q_{11} \\ q_{14} & -q_{13} & -q_{11} & q_{12} \\ q_{11} & q_{12} & -q_{14} & -q_{13} \\ -q_{12} & q_{11} & q_{13} & -q_{14} \end{bmatrix} \begin{bmatrix} \omega_{i\alpha}^p \\ \omega_{i\beta}^p \\ \omega_{i\gamma}^p \\ 0 \end{bmatrix} .
$$

(10d)

* Subsequent to the derivation of eq. (11) by Simmons, it was discovered that this same equation had been derived independently by Brown [13].
where
\[
\lambda = \sum_{i=1}^{N} \left( (p_i \cdot F_i - p_{p_i} \cdot \nabla u)/m + \sum_{\beta=1}^{3} \omega_{i\beta}^{p} T_{i\beta}^{p} \right) \times \left[ \sum_{i=1}^{N} \left( p_i^2/m + \sum_{\beta=1}^{3} I_{\beta} \omega_{i\beta}^{2} \right) \right]^{-1}.
\]

In eq. (11), \(T_{i\beta}^{p}\) is the torque on molecule \(i\) in the principal axis frame and so equals \(A_{i\beta} T\). We observe that for \(N\) molecules eqs. (9) and (10) constitute a set of \(13N\) first-order differential equations (with supplementary algebraic relations). The fourth-order predictor-corrector method of Gear [14] described in detail by Evans and Morriss [2] for Gaussian constrained translational motion is modified trivially to solve these equations of motion which represent the isokinetic slosh equations for a fluid of non-linear molecules. In section 2 of this paper, we describe the application of eqs. (9) through (11) to the NEMD simulation of methane. Results for the shear viscosity, hydrostatic pressure and configurational internal energy are reported in section 3.

### 2. NEMD simulation of methane

For the simulation of methane reported in this paper, the intermolecular potential of Williams [15] was used. This potential was developed for calculating liquid and solid state thermodynamic properties. It was evaluated by Murad et al. [16] and was found to be reasonably accurate in predicting the pressure, internal energy and diffusion coefficient of liquid methane. Maitland et al. [17] suggest that the Williams potential is the better one of the two potentials evaluated by them which explicitly include the anisotropic interaction between methane molecules. The potential is given by a sum of site-site interactions, viz.

\[
u(12) = \sum_{\alpha=1}^{5} \sum_{\beta=1}^{5} u_{\alpha\beta}(r_{\alpha\beta}),
\]

where \(r_{\alpha\beta}\) is the distance and \(u_{\alpha\beta}\) is the site-site potential between site \(\alpha\) on molecule 1 and site \(\beta\) on molecule 2. Each methane molecule has five sites (one carbon, four hydrogens) and each of the site-site potentials is an exponential-six potential:

\[
u_{\alpha\beta}(r) = A_{\alpha\beta} \exp(-B_{\alpha\beta} r) - C_{\alpha\beta} r^{-6}.
\]

The parameters in the site-site potential, which are determined by fitting solid state lattice energies, are given in table 1; the other quantities required to complete the specification of the interaction are the three moments of inertia of methane (which, due to the symmetry of the molecule, are equal to \(I_{xx} = I_{yy} = I_{zz} = 5.322 \times 10^{-40} \text{ g cm}^2\)), the \(\text{C-H bond length} = 1.026 \times 10^{-8} \text{ cm}\) and molecular mass \(m = 2.687 \times 10^{-23} \text{ g}\). The NEMD simulation is performed at the state point \(\rho = 0.288 \text{ g/cm}^3 (= 18.03 \text{ mole/l})\) and \(T = 285.7 \text{ K}\).

The force \(F_i\) exerted on the center of mass of molecule \(i\) is calculated as the sum of the forces acting on the sites in molecule \(i\) (obtained as the sum of site-site forces each of which is the gradient of the corresponding site-site potential). The torque \(T_i\) on the center of mass of molecule \(i\) is the sum of the torques due to the forces exerted on each site.

In order to calculate the shear viscosity, we require the expression for the pressure tensor \(P\) given by [3,18,19]

\[
P = m \sum_{i=1}^{N} (u_i - u)(u_i - u) + \sum_{i=1}^{N} r_i F_i,
\]

where \(V\) is the volume of the system and \(u\) is the streaming velocity. For a polyatomic fluid [18], the constitutive relation between the pressure tensor and the shear viscosity is

\[
P_{xy}^{0s} = -2\eta (\nabla u)^{0s}_{xy},
\]

where the notation \(A^{0s}\) denotes the symmetric, traceless part of the tensor \(A\). Applying eq. (15) to our system (in which the streaming velocity is given by \(u = (u_x, 0, 0)\)), we obtain as our equation for the shear viscosity

\[
\eta = (P_{xy} + P_{yx})/2\gamma.
\]
The hydrostatic pressure $p$ is, as usual, the trace of the pressure tensor.

3. Results

The NEMD simulations reported in this section were performed on a Computer Signal Processing Inc (CSPI) 6420 64-bit word array processor housed in the Center for Computer-Aided Engineering at the University of Virginia. All runs were performed using 125 methane molecules confined to a cubic simulation cell with the "sliding brick" boundary conditions described in section 1. The site-site pair potentials (13) were truncated at $3\sigma$ where $\sigma = 4.01 \times 10^{-10}$ cm. In order to speed up the force and energy calculations, these quantities were discretized onto a grid of 900 points equally spaced in $r^2$. To evaluate an energy of force between two sites, a linear interpolation in $r^2$ is performed.

At each strain rate, an initial run of 2000 timesteps was discarded as the system came to steady state from an initial simple cubic lattice. After this "equilibration", the simulation was run for 20000 time steps divided into ten blocks of 2000 time steps yielding ten "measurements" of the shear viscosity, hydrostatic pressure and configurational internal energy. These ten "measurements" were then regarded as independent and under this assumption their mean and standard deviation (recorded as a percentage) are reported in table 2. (Parenthetically, we should note that this method of estimating the errors in the simulation results is quite arbitrary since, for example, considering a smaller number of larger sized blocks would lead to lower standard deviations. In fact, we believe that the percentage errors given in table 2 and represented as error bars in the figures represent an overestimate of the error in the simulation results.)

From theoretical considerations [20–23] confirmed by extensive simulation studies [24–26], it has been determined that the strain rate dependences of the shear viscosity, hydrostatic pressure and configurational internal energy are given to leading order by

$$\eta = \eta_0 + \eta_1 \gamma^{1/2},$$

$$p = p_0 + p_1 \gamma^{3/2},$$

$$U_{\text{conf}} = U_0 + U_1 \gamma^{3/2}.$$  

In figs. 1 through 3, the shear viscosity, hydrostatic pressure and internal energy are plotted as functions of the strain rate $\gamma$. The circles and the error bars represent the simulation results and the estimated error respectively (see text for explanation). The straight line is the least-squares fit of the experimental data to eq. (17).

Table 2

<table>
<thead>
<tr>
<th>$\gamma$ (s$^{-1}$)</th>
<th>$\eta$ (poise)</th>
<th>$p$ (dyne cm$^{-2}$)</th>
<th>$U_{\text{conf}}/Nk$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6.757 \times 10^{11}$</td>
<td>$3.366 \times 10^{-4}$ (±7%)</td>
<td>$0.650 \times 10^6$ (±5%)</td>
<td>$-461.9 (+0.6%)$</td>
</tr>
<tr>
<td>$1.014 \times 10^{12}$</td>
<td>$3.312 \times 10^{-4}$ (±7%)</td>
<td>$0.716 \times 10^6$ (±5%)</td>
<td>$-456.7 (+0.6%)$</td>
</tr>
<tr>
<td>$1.350 \times 10^{12}$</td>
<td>$3.217 \times 10^{-4}$ (±5%)</td>
<td>$0.758 \times 10^6$ (±3%)</td>
<td>$-452.6 (+0.7%)$</td>
</tr>
<tr>
<td>$2.700 \times 10^{12}$</td>
<td>$2.995 \times 10^{-4}$ (±3%)</td>
<td>$1.018 \times 10^6$ (±3%)</td>
<td>$-430.4 (+0.6%)$</td>
</tr>
</tbody>
</table>

Fig. 1. The shear viscosity $\eta$ of methane at 285.7 K and 0.288 g cm$^{-3}$ as a function of the square root of the reduced strain rate $\gamma$. The circles and the error bars represent the simulation results and the estimated error respectively (see text for explanation). The straight line is the least-squares fit of the experimental data to eq. (17).
pressure and configurational internal energy are plotted as functions of $\gamma^{1/2}$, $\gamma^{3/2}$ and $\gamma^{3/2}$ respectively along with the appropriate least-squares fitted equations (17) through (19). It is clear that the simulation data do fit the proposed strain rate dependences. The zero-strain rate values of the viscosity, pressure and configurational internal energy are given by

\[ \eta_0 = 3.76 \times 10^{-4} \text{ poise}, \]
\[ p_0 = 6.11 \times 10^8 \text{ dyne cm}^{-2}, \]
\[ U_0/Nk = -465.5 \text{ K}. \]

Given the arbitrariness of the error estimates in the simulation runs, we have not attempted to estimate the error in these zero-strain rate extrapolation. The zero-strain rate shear viscosity represents the NEMD prediction for the Newtonian viscosity of methane at this state point. The experimental value reported by Evans [27] and attributed to Hanley et al. [18] is $3.77 \times 10^{-4}$ poise so that the theoretical result is within 1.3% of the experimental data. Evans [27] has previously simulated methane using the Williams potential at this state point using the earlier NEMD technique of Ashurst and Hoover [1] (rather than the slod algorithm used here) thermostatted by velocity rescaling at each time step (in contrast to the Gaussian thermostat employed in this paper). Evans obtained a value of $3.49 \times 10^{-4}$ poise which is within 10% of the experimental value. We attribute the improved accuracy of the Williams potential reported in this paper to the longer simulation runs and the higher efficiency of the isokinetic slod algorithm.

4. Discussion and conclusion

In this paper, we have demonstrated that the application of modern developments in NEMD simulation (slod dynamics constrained isokinetically via Gaus's principle) to molecular fluids is straightforward. The resulting algorithm is considerably more efficient than that previously applied to methane permitting longer simulation runs with lower fluctuations resulting in a more precise characterization of the shear viscosity. Our results suggest that the Williams potential is more accurate for viscosity at the supercritical dense fluid state simulated in this paper than was previously in-
Table 3
NEMD simulation results for the shear viscosity, hydrostatic pressure and internal energy as a function of strain rate $\gamma$ for a 108-molecule simulation of the LJ fluid at temperature 285.7 K and density 0.288 g cm$^{-3}$. The LJ parameters are given in the text and are appropriate to a simple fluid model of methane.

<table>
<thead>
<tr>
<th>$\gamma$ (s$^{-1}$)</th>
<th>$\eta$ (poise)</th>
<th>$p$ (dyne cm$^{-2}$)</th>
<th>$U_{conf}/Nk$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.378 \times 10^{11}$</td>
<td>$3.773 \times 10^{-4}$ (+4%)</td>
<td>$2.035 \times 10^{8}$ (+3%)</td>
<td>$-676.0$ (+0.2%)</td>
</tr>
<tr>
<td>$6.005 \times 10^{11}$</td>
<td>$3.703 \times 10^{-4}$ (+4%)</td>
<td>$2.128 \times 10^{8}$ (+5%)</td>
<td>$-672.8$ (+0.4%)</td>
</tr>
<tr>
<td>$9.382 \times 10^{11}$</td>
<td>$3.611 \times 10^{-4}$ (+3%)</td>
<td>$2.222 \times 10^{8}$ (+3%)</td>
<td>$-666.1$ (+0.3%)</td>
</tr>
<tr>
<td>$1.351 \times 10^{12}$</td>
<td>$3.407 \times 10^{-4}$ (+3%)</td>
<td>$2.341 \times 10^{8}$ (+5%)</td>
<td>$-662.5$ (+0.5%)</td>
</tr>
<tr>
<td>$1.839 \times 10^{12}$</td>
<td>$3.229 \times 10^{-4}$ (+2%)</td>
<td>$2.880 \times 10^{8}$ (+4%)</td>
<td>$-654.0$ (+0.2%)</td>
</tr>
</tbody>
</table>

One might reasonably ask whether it is necessary to use a full site-site potential for methane and still obtain agreement with experiment. In order to answer this question, we performed NEMD simulations on the Lennard-Jones (LJ) fluid which contains spherically symmetric molecules interacting with the pair potential

$$u(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6].$$

Maitland et al. [17] suggest that $\epsilon/k = 217$ K and $\sigma = 3.559$ Å are appropriate energy and diameter parameters which would permit methane molecules to be modelled as spherically symmetric and which would yield very good agreement with experimental measurements of the gas phase viscosity and the second virial coefficient. We have performed a series of NEMD simulation for the LJ fluid with these parameters with the results shown in table 3.

As in section 3, the simulation results were least-squares fitted to eqs. (17)–(19), yielding the following zero-strain rate extrapolations:

$$\eta_0 = 4.21 \times 10^{-4} \text{ poise},$$

$$p_0 = 1.93 \times 10^{8} \text{ dyne cm}^{-2},$$

$$U_0/Nk = -677.6 \text{ K}.$$  

Clearly, the viscosity is accurate to within about 12% of the experimental value using just a simple spherically symmetric potential. In view of the fact that a simulation of the Williams potential model for methane will typically consume twenty-five times more computer time than a LJ fluid simulation (due to the force/energy calculation), there will clearly be instances in which the lower accuracy of the simple fluid computation is more than compensated for by the decreased computation cost. On the other hand, there is a significant discrepancy between the thermodynamic predictions of the Williams and LJ potentials which only further simulations and comparisons with experiment can satisfactorily discriminate between.

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References

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