Nonequilibrium Molecular Dynamics Simulations of Planar Elongational Flow with Spatially and Temporally Periodic Boundary Conditions

B. D. Todd*

Cooperative Research Centre for Polymers, CSIRO Molecular Science, Private Bag 10, Clayton South MDC, Victoria 3169, Australia

Peter J. Daivis†

Department of Applied Physics, RMIT University, GPO Box 2476V, Melbourne, Victoria 3001, Australia

(Received 27 March 1998)

We apply the spatially and temporally periodic boundary conditions devised by Kraynik and Reinelt [Int. J. Multiphase Flow **18**, 1045 (1992)] to an atomic fluid undergoing planar elongational flow. The periodic boundary conditions guarantee theoretically infinite simulation times, and thus provide the most promising method yet developed to simulate molecular fluids undergoing steady planar extension using nonequilibrium molecular dynamics techniques. [S0031-9007(98)06571-5]

PACS numbers: 82.20.Wt, 61.20.Ja, 66.20.+d, 83.50.Jf

Extensional motion of fluids is a notoriously difficult rheological problem to study by use of nonequilibrium molecular dynamics (NEMD) techniques. Extensional, or elongational, flow occurs when a fluid is stretched in at least one direction, and compressed in at least one other. Such flows commonly occur in the processing of polymer melts, for example, where manufacturing techniques involve various forms of shear and extensional flows, such as planar shear flow, planar elongational, uniaxial and biaxial stretching flows, as well as combinations of these. Because of their immense technological relevance and their inherent scientific complexity, such flows are an extremely attractive field of study from a molecular perspective, and are highly suited for molecular simulation techniques in particular.

A few NEMD simulations on the steady (i.e., time-independent applied strain rate) elongational flow of simple atomic and molecular fluids have been performed in the past [1–5], but all suffered from one crippling limitation: the finite lifetime of a simulation due to the decrease of at least one of the simulation cell dimensions. Eventually the simulation must cease when the size of the cell in the contraction direction reaches its minimum extension of twice the range of the interaction potential. Thus, the fluid must achieve a nonequilibrium steady state well before this minimum size is reached for reasonable statistics to be obtained. This is not such a serious limitation for atomic fluids, but for molecular fluids with long relaxation times it is unlikely that relaxation to steady state will occur before the minimum cell size is reached [5].

To try to overcome these technical limitations, we previously studied a simple Weeks-Chandler-Andersen (WCA) [6] atomic fluid under the application of a frequency dependent strain rate [7,8], as well as by use of nonlinear response theory, via the transient time correlation function (TTCF) formalism [9,10]. In the former method, the simulation cell sinusoidally oscillates in time, guaranteeing that the system reaches a temporally periodic steady state. Time-independent steady-state quantities of interest, such as the elements of the pressure tensor and elongational viscosities, can be calculated by extrapolating the frequency dependent data down to zero frequency. In the latter method, the TTCF formalism was applied to planar elongational, uniaxial, and biaxial stretching flows. The advantage of TTCF is that it allows one to simulate fluids at extremely small strain rates with far superior statistics than that obtainable under direct timeaveraging. This in turn implies that a fluid can be simulated for much longer times than otherwise possible. Both techniques proved to be at least as accurate as the conventional NEMD method, and succeeded in significantlyextending the total available simulation time. Despite their successes, both methods are computationally more intensive than the conventional NEMD method, and their application to molecular fluids is yet to be attempted.

In this Letter we present the results of NEMD simulations of planar elongational flow using both spatially and temporally periodic boundary conditions. This method, first proposed by Kraynik and Reinelt [11], is remarkable in that it allows a conventional NEMD simulation to run for theoretically infinite simulation times. It rests upon the clever realization that a simulation cell which is initially oriented at certain discrete angles with respect to the direction of elongation can indeed be both spatially and temporally periodic. All previous NEMD simulations had always used periodic boundaries that were parallel to the flow fields. Such a rectangular geometry is doomed due to the technical limitation of minimum cell dimension, discussed above. Orienting the axes of the simulation cell at certain allowable angles to the flow field side steps this problem in a neat and elegant manner. The spatially periodic boundaries will now evolve in time such that they are (1) consistent with the applied strain rate, (2) compatible with the minimum image convention used in molecular dynamics simulations (the compatibility

 0031-9007/98/81(5)/1118(4)$15.00

condition of [11]), and (3) periodic in time (the reproducibility condition of [11]). NEMD simulations of steady elongational flow which use standard rectangular periodic boundary conditions satisfy conditions (1) and (2) above, but not (3). The limitation of applying the KR method is that it is only applicable to planar elongational flow. Kraynik and Reinelt proved that it could not be applied to either uniaxial or biaxial stretching flows.

Consider a square lattice which at $t = 0$ is oriented with respect to the direction of elongation at an angle θ, as depicted in Fig. 1(a). In our geometry, the fluid expands in the x direction with a strain rate $\dot{\varepsilon}$ and contracts in the y direction with the same strain rate (i.e., $-\dot{\varepsilon}$). As there is no flow in the z direction, we confine ourselves to a description of the geometry in the x-y plane only. Kraynik and Reinelt [11] were able to prove algebraically that such a lattice is spatially and temporally periodic only for certain discrete values of θ and the Hencky strain [11], defined here as $\varepsilon_p = \dot{\varepsilon}\tau_p$, where τ_p is the lattice strain period. This surprising result is difficult to obtain by geometric construction and is best arrived at algebraically. The reader should refer to their original work for the details, but we confine ourselves in this Letter to demonstrating that such a scheme can be successfully applied to NEMD simulations of planar elongational flow, even though their original work was confined to well-ordered lattice systems.

A lattice is reproducible if and only if there exist integers N_{ij} such that

$$\mathbf{L}_i(t) = \underline{\underline{\mathbf{\Lambda}}} \cdot \mathbf{L}_i(0) = N_{i1}\mathbf{L}_1(0) + N_{i2}\mathbf{L}_2(0) + N_{i3}\mathbf{L}_3(0), \quad (1)$$

where $i = 1, 2, 3$, $\mathbf{L}_i(0)$ are the initial linearly independent basis lattice vectors, and $\underline{\underline{\mathbf{\Lambda}}} = \exp(\nabla\mathbf{u}t)$, where $\nabla\mathbf{u}$ is the strain rate tensor, which will be defined shortly. The problem at hand reduces to one of determining which sets of integers make Eq. (1) valid. This in turn allows us to calculate θ and ε_p. We briefly summarize the procedure as follows:

(1) Choose any integer k, such that $k = 3, 4, 5 \ldots$

(2) Defining λ_p as $\lambda_p = \exp(\varepsilon_p)$, one can show that

$$\lambda_p = \frac{k \pm \sqrt{k^2 - 4}}{2}, \quad (2)$$

which in turn gives us the value of ε_p [i.e., $\varepsilon_p = \ln(\lambda_p)$]. Note also that $\varepsilon_p = \dot{\varepsilon}\tau_p$, as previously defined, which allows one to determine the lattice strain period τ_p for any desired values of ε_p and $\dot{\varepsilon}$.

(3) For the chosen value of k, choose a positive integer N_{11}, then solve for N_{12} using the expression

$$\left(N_{11} - \frac{k}{2}\right)^2 + N_{12}^2 = \frac{k^2}{4} - 1,$$

i.e.,

$$N_{12} = -\sqrt{N_{11}(k - N_{11}) - 1}. \quad (3)$$

(4) If and *only if* N_{12} is an integer (note: N_{12} is always taken as the negative root), then a solution has been found,

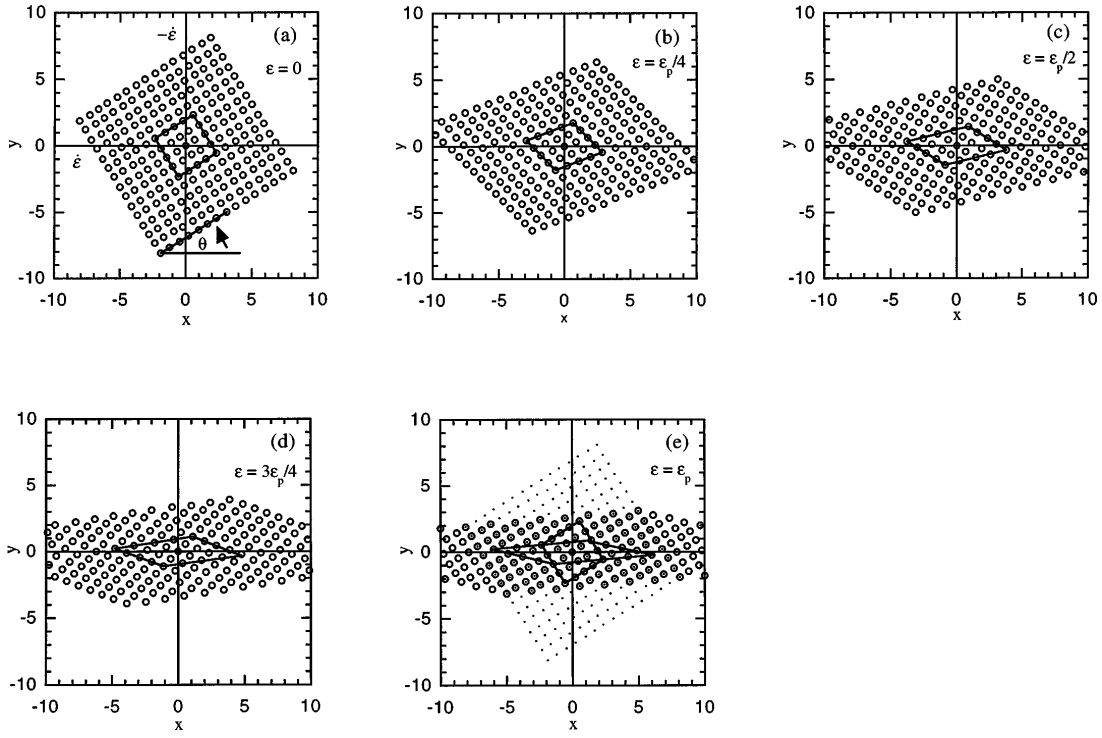

FIG. 1. Evolution of an fcc Kraynik-Reinelt lattice under planar elongational flow as a function of time. The orientation angle is $\theta = 31.7°$, and $\varepsilon_p = 0.9624$. At $\varepsilon = \varepsilon_p/2$, the lattice is the same as the original lattice, but with a different orientation. At $\varepsilon = \varepsilon_p$ the lattice reproduces itself. The fully extended (○) lattice is superimposed upon the original (●) lattice for comparison purposes.

and the "magic" angle θ is determined as

$$\theta = \arctan\left(\frac{N_{11} - \lambda_p}{N_{12}}\right). \tag{4}$$

Our NEMD simulations are based on the SLLOD equations of motion [7,12],

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla\mathbf{u}\,, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{p}_i \cdot \nabla\mathbf{u} - \alpha\mathbf{p}_i \end{aligned} \tag{5}$$

where the momenta are taken to be peculiar with respect to the streaming velocity $\mathbf{u}$, and $\nabla\mathbf{u}$ is the strain rate tensor, which for planar elongation is defined here as

$$\nabla\mathbf{u} = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{6}$$

α is a Gaussian thermostat multiplier used to constrain the system to constant temperature, given as

$$\alpha = \frac{\sum_i \mathbf{p}_i \cdot [\mathbf{F}_i - (\mathbf{p}_i \cdot \nabla\mathbf{u})]}{\sum_i \mathbf{p}_i^2}. \tag{7}$$

As elongational flow involves changes in the shape of the simulation cell, the periodic boundary conditions will evolve in time, such that the lengths of either all or some of the simulation cell dimensions decrease or increase with time. For the conventional case where the cell axes are parallel to the flow directions, the box shape evolves in time such that its shape is always rectangular. However, when the cell is aligned at an angle θ to the x-axis, the cell will evolve such that its shape is always a parallelogram, as depicted in Fig. 1. Integration of the equations of motion shows that all points on the cell boundaries evolve exponentially in time,

$$x(t) = x(0)\exp(\dot{\varepsilon}t)\,; \quad y(t) = y(0)\exp(-\dot{\varepsilon}t)\,. \tag{8}$$

This ensures that the dynamics are compatible with the evolution of cell boundaries, and that the system volume remains a constant of the motion.

Figures 1(a)–1(e) represent the evolution of a section of an infinite, initially square, fcc lattice structure under planar elongation. In this case $\theta \approx 31.7°$, and $\varepsilon_p \approx 0.9624$ (corresponding to $k = 3$, $N_{11} = 2$, $N_{12} = -1$), which guarantees that the system remains spatially and temporally periodic at times $t = n\tau_p$, where n is an integer. Also shown are the boundaries of the chosen unit cell, centered at the origin, and how they evolve with time over one Hencky strain period. Note that when $\varepsilon = \varepsilon_p/2$ the lattice is once again square, but with a different orientation to the $\varepsilon = 0$ case.

Of particular importance is what happens when $\varepsilon = \varepsilon_p$ (i.e., $t = n\tau_p$). Figure 1(e) shows that the lattice is now *identical* to the original lattice, upon which it is superimposed for clarity of comparison. In addition to this, the minimum lattice spacing, $D_{\min}$, of the unit cell is such that it is never less than the diameter of the particles. Thus, in the terminology used by Kraynik and Reinelt, the system is both reproducible (i.e., spatially and temporally periodic) and compatible (i.e., does not violate the minimum allowable lattice spacing).

Although Fig. 1 is descriptive of an ordered lattice, the same conclusions carry over to a disordered lattice, such as would be the case for an NEMD simulation. All one does in a simulation is to transform the cell boundaries at $t = n\tau_p$ (i.e., $\varepsilon = \varepsilon_p$) back to the original square lattice shape; i.e., all (x, y) points on the boundary are transformed as

$$x(t = n\tau_p) \rightarrow x(t = 0)\,; \quad y(t = n\tau_p) \rightarrow y(t = 0)\,. \tag{9}$$

As the periodic boundaries are now transformed to their initial $t = 0$ shape, one now applies normal periodic boundary condition rules to all the particles such that they too are transformed back into the square lattice. We describe this procedure in greater detail in a forthcoming paper [13], in which we will demonstrate how to apply an extremely efficient algorithm to perform this. This algorithm proves to be for planar elongation what Lees-Edwards boundary conditions are for planar shear. One must also ensure that throughout the simulation $D_{\min} > 2r_c$, where r_c is the interaction potential radius cutoff. This will be the case, no matter what orientation angle and Hencky strain one chooses, as long as the size of the simulation cell is sufficiently large.

We present the results of two simulations, one for a system of $N = 864$ atoms, and the other for a system of $N = 2048$ atoms. In the former, we have used $\theta = 31.7°$, and $\varepsilon_p = 0.9624$, while in the latter $\theta = 22.5°$, and $\varepsilon_p = 1.7627$ [see Eqs. (1)–(4) above, as well as Table I, Ref. [11] for these parameters]. In both simulations the strain rate was $\dot{\varepsilon} = 0.5$. All atoms interact via the WCA potential of Weeks, Chandler, and Andersen [6] defined as $\phi(r) = 4(r^{-12} - r^{-6}) + 1$ for $r < 2^{1/6}$; $\phi(r) = 0$, for

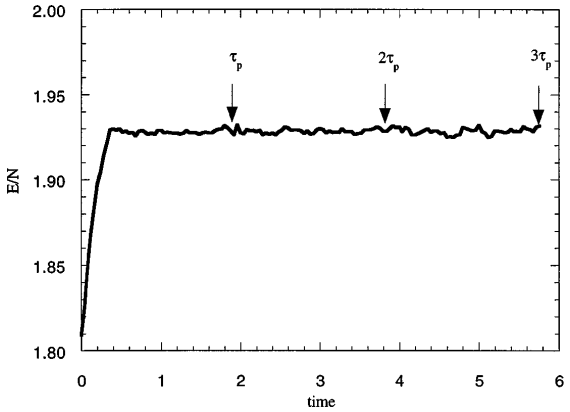

FIG. 2. Total internal energy per particle as a function of time for a Kraynik-Reinelt cell of $N = 864$ particles undergoing planar elongational flow. $\theta = 31.7°$, $\varepsilon_p = 0.9624$, and $\dot{\varepsilon} = 0.5$. The total simulation time is $3\tau_p$, where $\tau_p = 1.92$. All units are reduced and dimensionless, unless otherwise specified.

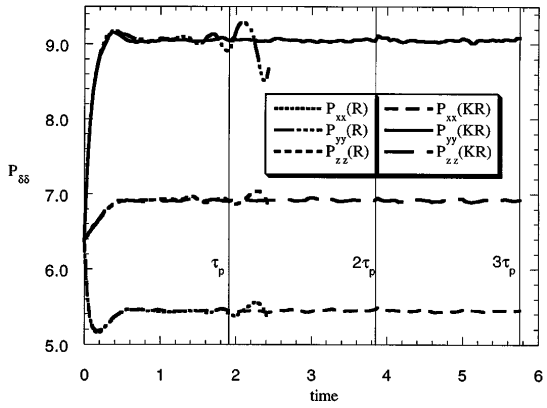

FIG. 3. Diagonal elements of the pressure tensor for the Kraynik-Reinelt cell (KR) of Fig. 2. Also displayed are corresponding conventional rectangular simulation cell results (R) for planar elongational flow.

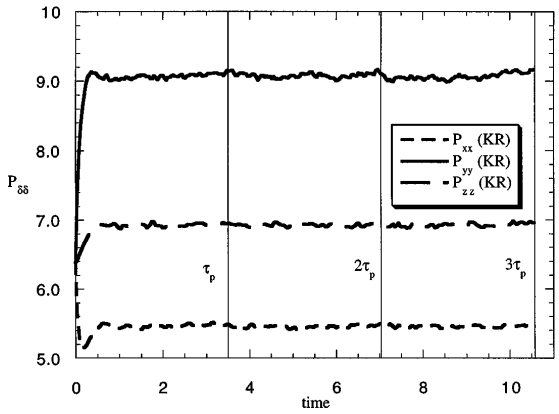

FIG. 4. Diagonal elements of the pressure tensor for a KR cell of $N = 2048$ atoms, with $\theta = 22.5°$, $\varepsilon_p = 1.7627$, and $\dot{\varepsilon} = 0.5$. The total simulation time is $3\tau_p$, where $\tau_p = 3.52$.

$r > 2^{1/6}$, where we define the WCA potential constants σ and ε, as well as the mass of the atoms, to be unity for simplicity. All simulations are performed at the Lennard-Jones triple point, $\rho = 0.8442$ and $T = 0.722$ in reduced units. The equations of motion were integrated using a 4th order Runge-Kutta scheme, and the integration timestep was 0.004 in reduced units for all simulations.

Figure 2 shows the total internal energy per particle as a function of time for the $N = 864$ system. The total simulation time is $3\tau_p$, though in principle a simulation can run for infinite time. The energy is clearly seen to be continuous, especially at the critical times of τ_p, $2\tau_p$, and $3\tau_p$, when the simulation cell undergoes its transformation back to the $t = 0$ configuration. Any lack of reproducibility would have immediately manifested itself in discontinuity in the energy at these times. The fact that this is not observed, and that the energy remains essentially constant after steady state has been achieved, suggests that the method works extremely well.

In Fig. 3 the diagonal elements of the pressure tensor are plotted as a function of time for the same system. In addition, we plot the diagonal elements of the pressure tensor for a similar system of $N = 864$ particles under a conventional NEMD simulation, in which the rectangular simulation cell in the *x-y* plane is aligned with the flow directions. Such a simulation must cease when the length of the cell in the contracting *y* direction reaches its minimum of $2r_c$. This corresponds to a time of $t_{\max} = -\dot{\varepsilon}^{-1} \ln(\frac{2r_c}{L_y(0)})$, or ≈ 2.4 in the geometry used. Agreement between both results is excellent, with the KR geometry having the obvious advantage of no maximum simulation time. Of further interest in this comparison is the lack of observable oscillations in the new method. These oscillations have been previously observed for the rectangular geometry [7,10], and it has been suggested that they are a consequence of strong correlations between particles when the length of the cell in the contracting dimension is of the order $\sim 2r_c$. However, in the skewed KR geometry $D_{\min} \sim 4r_c$, which suggests that the minimum lattice spacing is sufficiently large that particle correlations are unable to have a strong influence on any of the thermodynamic properties we computed.

Finally, in Fig. 4 the diagonal elements of the pressure tensor for a system of $N = 2048$ particles are shown, with an orientation of $\theta = 22.5°$, and $\varepsilon_p = 1.7627$. The excellent agreement with the corresponding results in Fig. 3 suggests that the method should work well for any of the possible orientations allowed by Eqs. (1)–(4). We note here that the system size needed to be much larger than the $N = 864$ system to ensure that $D_{\min} > 2r_c$.

We wish to acknowledge Professor John Brady, Division of Chemistry and Chemical Engineering, Caltech, who kindly informed us of the work of Kraynik and Reinelt.

*Email address: b.todd@molsci.csiro.au
†Email address: p.daivis@rmit.edu.au

[1] D. M. Heyes, Chem. Phys. **98**, 15 (1985).
[2] M. W. Evans and D. M. Heyes, Mol. Phys. **69**, 241 (1990).
[3] M. N. Hounkonnou, C. Pierleoni, and J.-P. Ryckaert, J. Chem. Phys. **97**, 9335 (1992).
[4] A. Baranyai and P. T. Cummings, J. Chem. Phys. **103**, 10 217 (1995).
[5] M. Kroger, C. Luap, and R. Muller, Macromolecules **30**, 526 (1997).
[6] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).
[7] B. D. Todd and P. J. Daivis, J. Chem. Phys. **107**, 1617 (1997).
[8] P. J. Daivis and B. D. Todd, Int. J. Thermophys. (to be published).
[9] B. D. Todd, Phys. Rev. E **56**, 6723 (1997).
[10] B. D. Todd, Phys. Rev. E (to be published).
[11] A. M. Kraynik and D. A. Reinelt, Int. J. Multiphase Flow **18**, 1045 (1992).
[12] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic Press, London, 1990).
[13] B. D. Todd and P. J. Daivis (to be published).