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Citation: *The Journal of Chemical Physics* **110**, 42 (1999); doi: 10.1063/1.478082

View online: <http://dx.doi.org/10.1063/1.478082>

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Steady state simulation of planar elongation flow by nonequilibrium molecular dynamics

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(Received 2 July 1998; accepted 29 September 1998)

We present a novel method for performing steady state nonequilibrium molecular dynamics simulation of planar elongation flow based on the studies of Kraynik and Reinelt [Int. J. Multiphase Flow **18**, 1045 (1992)]. These authors identified the orientation of the unit cell which leads to periodic behavior of the square lattice with the minimum period. This way the exponential deformation of the system periodically returns to a state where replacing some of the original particles with their images the initial state boundaries are recovered. We adopted their theoretical results to nonequilibrium molecular dynamics simulations and performed representative calculations for simple fluids. The new method solves the long-standing problem of simulating planar elongation flow in the steady state. © 1999 American Institute of Physics. [S0021-9606(99)51901-6]

I. INTRODUCTION

Two classes of viscometric flows, shear and shear-free flows, are used to characterize the rheological properties of polymeric fluids.¹ In recent years computer simulation studies have been performed to help the microscopic understanding of these complex systems.² However, with the exception of a handful of studies,^{3–6} computer simulation deal overwhelmingly with shearing fluids. This disparity is caused by practical problems of implementing elongation flow simulations. In the case of planar Couette flow, the periodic boundary conditions of the nonequilibrium molecular dynamics (NEMD) algorithm make possible an arbitrarily long steady state simulation of the system,² while in elongation flows [planar elongation flow (PEF), biaxial stretching flow (BSF), and uniaxial stretching flow (USF)] (Ref. 1) the exponentially fast deformation of the simulation box sets a limit on the time range available for study. To obtain steady state values of system properties one should maintain a constant elongation rate (i.e., exponential change in system dimensions) for a sufficiently long time to expect transients to become negligible. During this time, however, the smallest system diameter should be larger than certain reasonable minimum so that the simulated system is not reduced to molecular dimensions in any direction. This requires large systems, particularly for high elongation rate simulations.

A trivial way to reduce the demand for large systems is to change the simulation cell from the usual cube to a brick shape which has the smallest starting dimension in the direction of expansion and vice versa. This method was invoked in earlier simulations to reduce the cost of the calculations.^{3–5} In addition to these approaches, the present authors proposed a simple scheme of increasing the total simulation time by effectively doubling the cell length in the contracting direction when it gets close to the minimum acceptable length.⁵ This was accomplished by defining one set

of images as real particles and adding random displacements to their positions and velocities. Since the overall system is a nonlinear dynamical system, the phase space trajectories of the new particle will be uncorrelated with the original particles after a characteristic time determined by the magnitude of the largest Lyapunov exponent. However, if the elongation rate is very high, there is no time for the new particles to evolve along a substantially different trajectory.

Todd and Davis proposed a different approach to overcome the difficulties of elongation flow simulations.⁶ This technique involves simulating elongation flow by applying a frequency-dependent strain rate that ensures that the system attains a temporally periodic steady state. For a given magnitude of the strain rate, quantities of interest, such as the diagonal elements of the pressure tensor, and hence elongation viscosities, are then calculated by extrapolating their frequency-dependent values down to zero frequency.⁶ However, while this technique may be applicable to simple fluids, it is unlikely to be successful for systems in which the establishment of steady-state flow is accompanied by significant changes in the structure of the fluid. This would involve the technologically important class of chain molecules, including alkane liquids and polymers.

In this paper we describe a method which is capable of simulating steady elongation flow directly for arbitrary molecular systems without any ambiguity inherently present in previous approaches described above. This technique is based on the studies of Kraynik and Reinelt.⁷ Using rigorous mathematical formulation, these authors investigated the change in the spatially periodic microstructure of a fluid under the impact of elongation flow. They found periodic behavior for PEF and showed that no lattice exhibits such characteristics for USF and BSF. Independent development of the Kraynik–Reinelt boundary conditions to the elongational flow of suspensions is described by Claeys.⁸ Further applica-

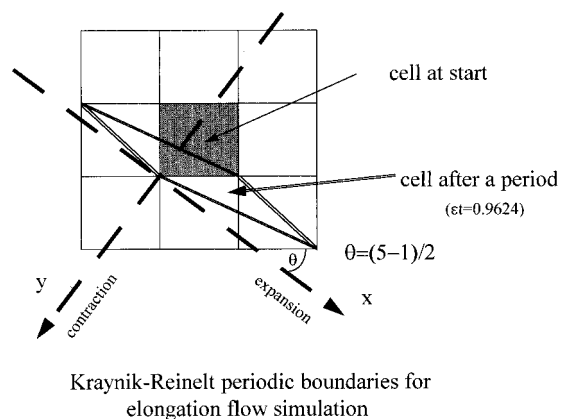


FIG. 1. Orientation of the simulation cell at the start (surrounded by the images) and the cell after a period (double lines).

tion of the Kraynik-Reinelt boundary conditions to the elongational flow of suspensions is described by Sami.⁹

In Sec. II, we describe the important implications of Kraynik and Reinelt's work for NEMD simulations, and present representative calculations in Sec. III.

II. OPTIMUM PERIODIC CONDITIONS FOR STEADY PLANAR FLOW

The most important outcome of Kraynik and Reinelt's work for our purposes was the determination of an orientation angle for a regular square lattice⁷ at which elongation flow is periodic with a minimum period. The smallest period is obtained if the orientation angle of the square lattice (which in our case represents the usual periodic boundary conditions of computer simulations) is θ , where $\tan \theta = (\sqrt{5} - 1)/2$. In Fig. 1 we show the arrangement. The expansion is parallel with the x -, the contraction with the y -axis. The central square represents the simulation cell at start. The nearest images can be found in the other 8 boxes surrounding the central one. As time goes the shape of the simulation cell changes. After $\epsilon t \cong 0.9624$ (where ϵ is the elongation rate and t is the time) the shape of the cell is given by the parallelogram represented by double lines. It is easy to see that this box contains exactly one image of each particle, i.e., it corresponds to a different but completely equivalent description of the same periodicity.

There can be several other realizations of this scheme.⁷ However, it is the one with the smallest period which has the largest final distance between the contracting parallel lines of the box. The value of this distance is $(1/\sqrt{5})L$, where L is the length of the initial box. This distance should be at least double the interaction cut-off between particles.

The practicalities of our calculations are the following. The x , y , and z coordinates of the particles represent their "real" positions. The SLLOD equations of the elongation flow,⁵ the calculation of forces, pressure tensor elements, etc., are also carried out in this reference system. However, the x and y positions are also expressed in terms of the frame of the actual unit cell geometry. The role of these a and b positions is to find the nearest image of the interacting particles. Since the shape of the unit cell changes constantly, the x and y coordinates of the particles are transformed into a

TABLE I. Results of the WCA simulations $\eta = (p_{yy} - p_{xx})/4\epsilon$. (See the text for further details.)

ϵ	U/N	p_{xx}	p_{yy}	p_{zz}	η
0.0	1.812	6.400	6.400	6.400	...
0.05	1.817	6.246	6.670	6.400	2.12
0.05*	1.819	6.135	6.621	6.403	2.43
0.1	1.823	6.086	6.904	6.436	2.05
0.1*	1.821	6.054	6.915	6.426	2.15
0.2	1.843	5.898	7.394	6.545	1.870
0.4	0.900	5.693	8.442	6.798	1.718
0.5	1.937	5.640	9.010	6.966	1.685
0.8	2.066	5.630	10.72	7.550	1.591
1.0	2.182	5.730	12.04	8.060	1.578
1.6	2.65	6.475	16.60	10.11	1.582
2.0	3.10	7.380	20.41	11.94	1.629
2.5	3.83	8.960	25.94	14.83	1.698
3.2	5.34	12.18	36.65	20.64	1.912

and b ones in every time step and vice versa. Once the system completed a period we can redefine the unit cell and continue the simulation.

Since the length of the period is not an integer it is advised to define a time step in terms of the following relationship: $\epsilon \times \Delta t \times M = 0.9624$, where Δt is the time step and M is an integer indicating when the reformulation of the unit cell is necessary.

III. DETAILS AND RESULTS OF THE CALCULATION

We studied two models of simple systems; the Lennard-Jones liquid and the WCA fluid. Particles of the latter are defined by a short-range version of the Lennard-Jones interaction. The pair-potential, $\phi(r)$, is also spherically symmetric, pairwise additive and is given in terms of the distance between two particles, r , as follows:

$$\phi(r) = \begin{cases} 4[r^{-12} + r^{-6}] + 1 & r < 2^{1/6} \\ 0, & r > 2^{1/6} \end{cases}.$$

Here we used the usual reduced units of computer simulations.⁹ The number density, $\rho = 0.8442$, and the temperature, $T = 0.722$, corresponds to triple point conditions of liquid argon. At this density 108 WCA particles are sufficient to perform the calculations consistently but in the case of the Lennard-Jones potential with the usual cut-off of 2.5, we had to use a much larger system which contained 1372 particles. Tables I and II show the results for the WCA and

TABLE II. Results of the LJ simulations. $\eta = (p_{yy} - p_{xx})/4\epsilon$. (See the text for further details.)

ϵ	U/N	p_{xx}	p_{yy}	p_{zz}	η
0.0	-5.007	0.148	0.148	0.148	...
0.1	-4.984	-0.274	0.827	0.241	2.75
0.2	-4.943	-0.460	1.475	0.410	2.42
0.5	-4.791	-0.690	3.326	1.002	2.01
0.8	-4.598	-0.650	5.266	1.719	1.85
1.0	-4.441	-0.518	6.694	2.312	1.80
1.6	-3.855	0.409	11.349	4.513	1.71
2.0	-3.372	1.364	14.959	6.354	1.70
2.5	-2.577	3.014	20.528	9.381	1.75

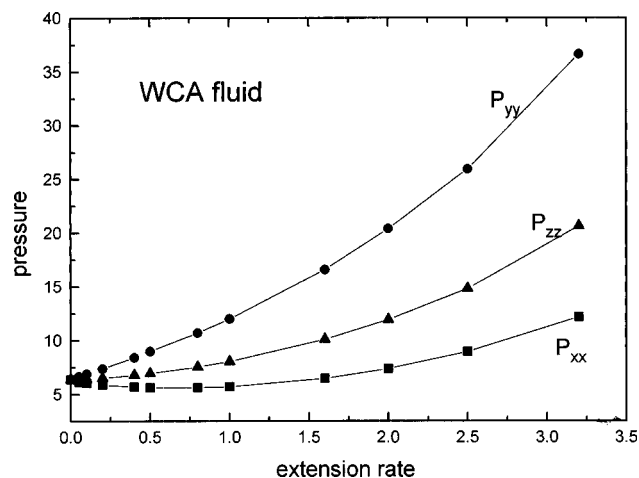


FIG. 2. Diagonal pressure tensor elements in terms of the elongation rate for the WCA fluid.

for the Lennard-Jones system, respectively. In Table II both the internal energy per particle (U/N) and the diagonal elements of the pressure tensor (p_{xx} , p_{yy} , and p_{zz}) contain long-range corrections.¹⁰

We applied the Gaussian thermostat (differential feedback)² independently in the three directions, i.e., we maintained the 0.722 target temperature in the x -, y -, and z -directions separately. Clearly, this means different heat removal in different directions. The usual method has identical thermostating multipliers which produce large differences in the random kinetic energies along the three coordinate axes. The difference between the results of these two possibilities is not very large in shear viscosity, because the kinetic part of the off-diagonal pressure tensor elements is small.¹¹ It is quite substantial, however, in elongation flows where viscosities are manifested via diagonal elements of the pressure tensor.¹² This is the reason that our viscosities are somewhat smaller than our previous results for PEF where we used the uniform multiplier approach.⁵ As a check against programming errors we calculated the viscosities by

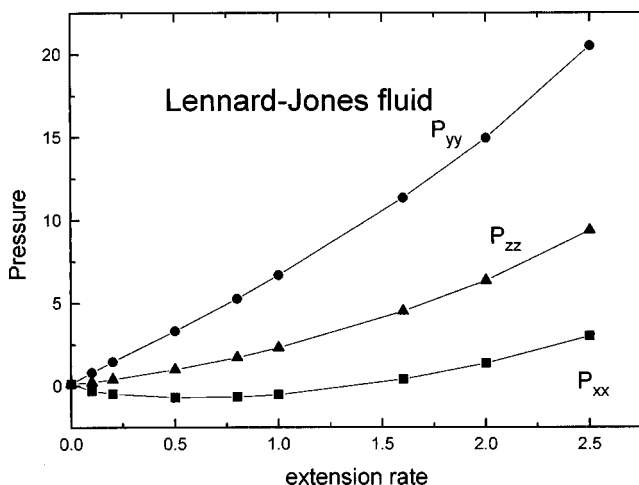


FIG. 3. Diagonal pressure tensor elements in terms of the elongation rate for the Lennard-Jones fluid.

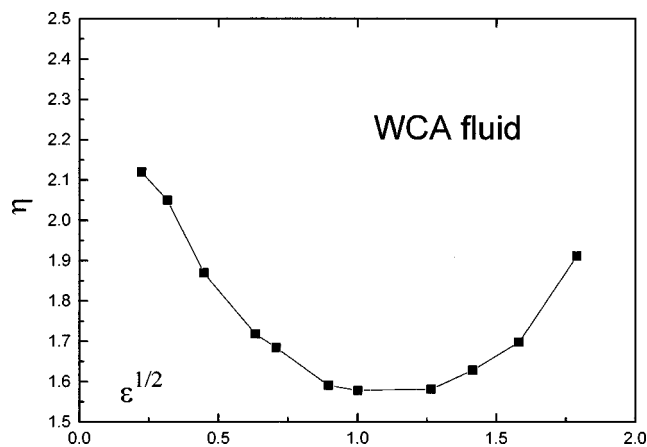


FIG. 4. Elongation viscosities in terms of the square root of the elongation rates for the WCA fluid. The extrapolated linear used only four values of the smallest elongation rates.

the latter method for the two small elongation rates (marked by stars in Table I) and obtained results in agreement with our previous calculations.⁵

In Figs. 2 and 3 we show the diagonal elements of the pressure tensor for the two systems. In Figs. 4 and 5 the elongation viscosity is presented in terms of the square root of the elongation rate. As could be expected, the qualitative behavior of the two systems are very similar. At low elongation rates both systems show elongation thinning as you might expect from the rotational correspondence of planar Couette flow and planar elongation flow in the linear regime.⁵ At high elongation rates this turns into elongation thickening. This behavior can be observed for certain polymer melts experimentally and can be predicted by theories of Hookean dumbbells and Lodge's rubberlike liquid.¹ Nevertheless, knowing the extremely high elongation rate in our simulations ($\sim 10^{12}$ Hz if one identifies the Lennard-Jones system with liquid argon) and the fairly simple structure of the fluid, we think the cause of elongation thickening is the jamming of particles.

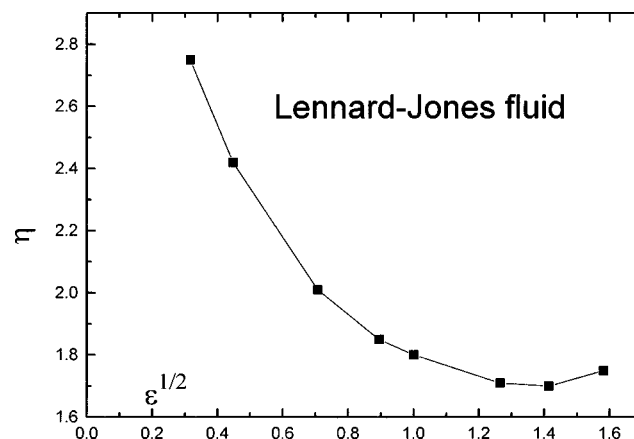


FIG. 5. Elongation viscosities in terms of the square root of the elongation rates for the Lennard-Jones fluid.

IV. CONCLUSIONS

The most important conclusion of this work is that it is possible to simulate steady planar elongation flow using a finite number of particles. The efficiency of the method is not as good as that of planar Couette flow but the calculation can be continued for an infinitely long time with arbitrary elongation rates. Unfortunately, there is no similar possibility for the two other shear-free flows.⁷ The absence of an apparently steady-state method is not as severe for USF because in the case of USF the expansion of one direction is accompanied with the contraction of two directions. As a result the existing method work reasonable efficiently for USF.

Our calculations again highlighted the problem of temperature definitions away from equilibrium.¹³ Since these simple models provide only a qualitative picture, the role of the thermostat is not crucial. However, in the case of comparisons of numerical results the complete definition of the system requires a detailed description of the thermostatting mechanism.

Note added in proof. It has come to our attention that the paper by B. D. Todd and P. J. Daivis [Phys. Rev. Lett. **81**, 1118 (1998)] also exploits the Kraynik–Reinelt solution.

ACKNOWLEDGMENTS

The authors acknowledge the support of the NSF-MTA Collaborative Research Program through Grant No. INT-

9603005. A. B. also acknowledges the support of OTKA Grant No. T24042. The authors are particularly indebted to John Brady of Caltech who pointed to one of us (P.T.C.) the Kraynik and Reinelt paper (Ref. 7). We thank an anonymous reviewer for bringing Refs. 8 and 9 to our attention.

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