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Multiscale modeling of polymer rheology

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We propose a simulation method which can be used to readily parallelize simulations on systems with a large spatial extent. We simulate small parts of the system with independent molecular dynamics simulations, and only occasionally pass information between them through a constitutive model free continuum approach. We illustrate the power of this method in the case of a polymeric fluid undergoing rapid one-dimensional shear flow. Since we show that this flow problem cannot be modeled by using a steady-state constitutive model, this method offers the unique capability for accessing the nonlinear viscoelasticity of complex fluids.

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An important goal for conventional computer methods is to simulate large enough systems so as to approach the truly macroscopic limit. However, such efforts are limited by the fact that even though computational requirements per step scale nearly linearly with system size, the system relaxation time typically scales as the number of particles squared. Current methods designed to attain this goal partition the computational effort between several computers: information between the different CPUs is then often exchanged through message passing [1–3]. Since message passing is strongly limited by communication latency, the simulation of large scale systems have generally been out of reach. Instead researchers have attempted to circumvent these problems by performing full-fledged atomistic simulations for a part of the system (which has large property gradients), and using a continuum approach for the rest. The question lies in how the two parts would communicate, and a variety of prominent scholars have recently focused on solving this issue [4–9].

Here we propose an information passing multiscale approach aimed at significantly reducing the cost of conducting MD simulations on large systems. In contrast to past methods, we simulate each part of the representative system through independent MD simulations with periodic boundary conditions. We, then, very occasionally communicate between these MD simulations through the use of a continuum method. Since the proposed method is shown to accurately represent the systems of interest, and since it does not employ a constitutive model, it can be applied to highly nonlinear flow situations, involving memory effects, where methods employing *steady-state* constitutive models may be expected to be inadequate.

Our proposed scale bridging idea is sketched schematically in Fig. 1 for the illustrative example of a polymer melt undergoing one-dimensional oscillatory shear flow. As sketched in Fig. 1, we break up the y direction using $(N+1)$ grid points. There are thus two scales in the problem, the fine scale (or gauss point) and the full system (coarse grained problem). Each gauss point is modeled by an *independent* molecular dynamics (MD) simulation with Lees-Edwards periodic boundary conditions. There is a velocity profile imposed along the y direction of each cell, with this being input from the coarse grained problem. The MD simulations are run for a certain (long) time, Δt, which corresponds to the time scale of the coarse grained integrator. The MD simulations calculate transient stresses over this time scale, which are then used by a continuum, "Navier-Stokes" type equation to advance the time of the large system and yield a new velocity profile. The process then repeats. Since the message passing between the gauss point MD simulations and the full scale macro problem happens very occasionally, the problems encountered by traditional parallel schemes are significantly reduced [1,2,4–8,10–27]. We shall conclusively show that the scale bridging approach allows us to model an oscillatory shear experiment, where the time scale of the oscillation is much faster than the chain relaxation time. Over these time scales the use of a constitutive model is found to be inadequate, thus clearly motivating the use of these multiscale, bidirectional information passing schemes.

Mathematically, we describe this scale bridging approach through a Lagrangian framework since we desire to incorporate memory effects, and the consequent dependence of

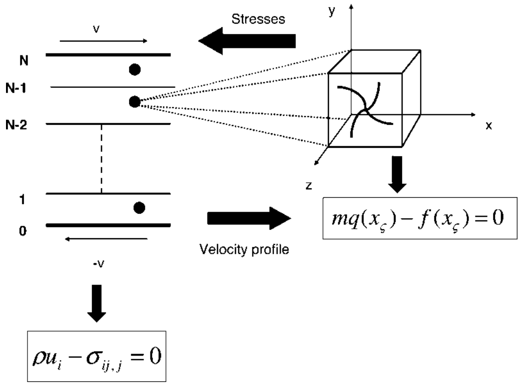

FIG. 1. Schematic representation of the proposed multiscale method. The stresses calculated from the MD simulations are used in the coarse grained methods, while the coarse grained methods yield velocity profiles which are used in the next set of MD simulations.

properties on the overall deformation. Following the generalized mathematical homogenization (GHM) theory [28,29], the governing equations for the fine scale problem, the scale bridging equation and the coarse grained problem are:

$$\begin{aligned} &m\ddot{q}(\mathbf{x}_\zeta) - \mathbf{f}(\mathbf{x}_\zeta) = 0 \text{ on } \Theta_\zeta \cdots \text{fine scale (MD)} \\ &\sigma(\mathbf{x}_\zeta) = \frac{1}{2\Theta_\zeta}\sum_A \sum_{B\neq A} \mathbf{r}_\zeta^{\mathbf{AB}}(\mathbf{x}_\zeta) \\ &\qquad \otimes \mathbf{f}_\zeta^{\mathbf{AB}}(\mathbf{x}_\zeta) \cdots \text{scale bridging (modified virial)} \\ &\rho\ddot{u}_i - \sigma_{ij,j} = 0 \text{ on } \Omega \cdots \text{coarse scale (continuum)} \end{aligned} \tag{1}$$

where ρ is the density of the fluid, $u_i(\mathbf{x})$ the continuum displacement, $\sigma(\mathbf{x})$ is the continuum Cauchy stress tensor [σ_{ij} is the i-jth component], $q(\mathbf{x})$ is the displacement vector, m the atom mass, $\mathbf{f}(\mathbf{x})$ the force vector, Ω and Θ_ζ the coarse grained and fine grained domains corresponding to the gauss point positioned at $\mathbf{x}_\zeta$, respectively. The standard summation convention over repeated indices in assumed.

Large system simulations: The large system whose behavior we want to model corresponds to a box of size 14.1σ on a side in the x and z directions, while the y direction is 282σ (σ is the monomer size, see below). These results will provide the benchmark against which the proposed method will be calibrated. We conducted molecular dynamics simulations on a polymer melt in this box under the action of an oscillatory shear flow. Each polymer chain is modeled by 120 beads connected by FENE springs [30]. All beads interact with a shifted, purely repulsive Lennard-Jones potential $U_{\mathrm{LJ}}(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]+\epsilon$ for $r<2^{1/6}\sigma$ and $U_{\mathrm{LJ}}(r)=0$ for $r>2^{1/6}\sigma$. We report only reduced variables, with σ, $\tau=\sigma\sqrt{m/\epsilon}$ and m representing the units of length, time, and mass, respectively (m is the monomer mass.) We consider a monomer number density of $\rho\sigma^3\approx 0.85$. Standard periodic boundary conditions are assumed along the x and z directions, while we employ the Lees-Edwards boundary condition along the y direction: the one-dimensional oscillatory shear flow corresponded to the x component of the velocity alone, v_x, varying in the y direction. The time dependent velocities at the top and bottom boundaries have the form $v^*=\pm v_0^*\sin(\omega t^*)$ where the positive velocity is assumed at the top boundary while the negative velocity is imposed at the bottom boundary. $\omega=2\pi/T^*$, $T^*=320$ being the time period for oscillation. At the end of every MD time step only the y and the z components of particle velocities are rescaled according to the given temperature [31,32]. The integration was performed at a constant temperature of $T_0^*=(k_BT_0/\epsilon)=1$ and a time step of $\delta t^*=0.0008$.

Scale bridging simulations: In the proposed method each gauss point is represented by a cube of size 14.1. We enforce a linear velocity profile along the y direction, which is consistent with the instantaneous shear rate predicted by the coarse grained simulations. The integration time steps are $\delta t^*=0.0008$, where $\delta t \ll \Delta t$ and also $\Delta t \ll T$ (Δt is the integrator time step for the coarse grained problem). The nonequilibrium MD simulations employ the fifth-order predictor-corrector algorithm [31]. All three components of particle velocities are rescaled after every MD time step. The starting configurations for each of these gauss points is taken to be the same as the ending configuration of the simulation corresponding to the previous coarse time step in order to properly take memory effects into account. A second option we have considered is to use a completely random starting configuration for each gauss point simulation.

However, as we shall show below, this second class of simulations provides a poor agreement between the scale-bridging and the full scale MD simulation, since it does not capture memory effects. The coarse scale equations are typically integrated using explicit methods with a time step $\Delta t^*=0.08$, and we emphasize that we employed the simplest finite difference form of these equations. (Thus, message passing is conducted after 100 MD steps of the gauss point MD simulations.)

Results: Figure 2 compares the results of the velocity profile across the simulation box as obtained from the full MD simulations as well as the multiscale method. Clearly, there is excellent agreement between the two across all times conclusively proving that the proposed method allows for an accurate simulation of these relatively fast shear flows whose time constant $T^*=320$ is about 50 times shorter [33] than the relaxation times of the chains in question. In these figures we also show results where the gauss points do not retain memory: that is we reinitialize the configurations of the gauss points after each integration step of the continuum equations. It is apparent that this method does not yield accurate results, restressing the importance of memory effects in this problem. This implies that each MD simulated gauss point has to be followed for the whole duration of the simulation. Thus with all gauss points simulated by MD there is no time scale advantage. We will address this issue below.

Another fact which further stresses the importance of the memory effects is discussed here. Following the early work of Kroger and Hess [34] we know that polymeric fluids are shear thinning. Since we know the strain rate dependent viscosity, we can use this constitutive equation in combination with the relationship: $\sigma_{xy}=\eta\frac{\partial v_x}{\partial y}$ as the definition of the stress. The coarse grained problem can then be solved without resort to the grid point simulations. Figure 2 clearly shows that this approach also fails to reproduce the velocity profile obtained from the large system simulation. We attribute this failure to the fact that chains in steady shear flows (which are used to generate the constitutive model) are strongly stretched in the direction of flow, which then leads to shear thinning behavior. In contrast, for the fast oscillatory shear flows considered here, the chain conformations are not able to track the velocity profiles. Figure 3, which plots the mean-squared x-component of the end-to-end vector of the chains in steady shear and our oscillatory shear condition starting from rest, verify this notion.

In addition to providing an accurate means of providing communication between different parts of a large simulation cell, we note that the proposed method also can be used in a scale bridging sense. To illustrate this point we have simulated two other systems which continue to be 14.1 in the x and z directions, but with sizes of 564 and 846 in the y direction. These are simulated under the action of oscillatory shear but with larger time periods of $T^*=800$ and 1600, respectively. In these cases we continue to employ only 20 equidistant gauss points, and even as few as 10 gauss points

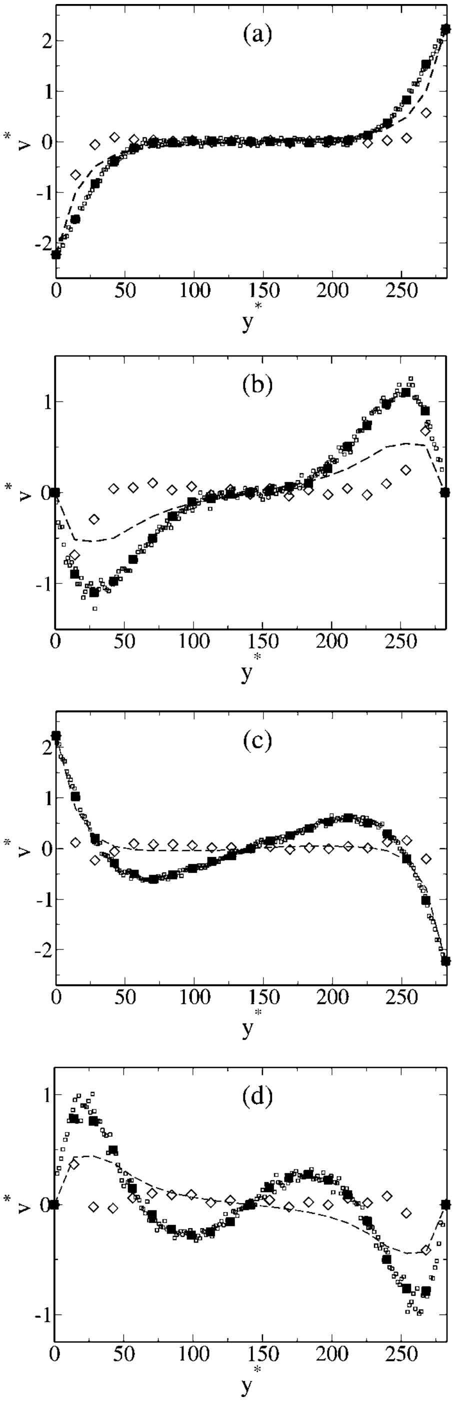

FIG. 2. Velocity profiles obtained for system thickness 282σ for times (a) $t^*=80$, (b) $t^*=160$, (c) $t^*=240$, and (d) $t^*=320$, using direct MD (small hollow squares), the proposed multiscale method (filled squares), freshly equilibrated configurations before every coarse time step (hollow rhombi), and the steady-state constitutive equation (broken line).

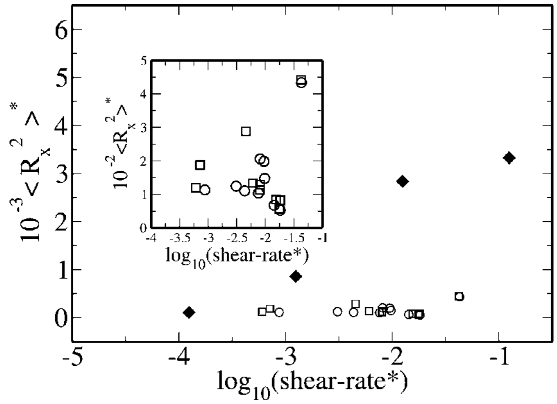

FIG. 3. Mean-squared end-to-end x-vector of chains as a function of shear rate, for the steady state (filled rhombi), and for times $t^*=320$ (hollow squares) and $t^*=640$ (hollow circles) for the multiscale method. The inset shows more clearly the data for only the multiscale method.

for the larger system, using a coarse time step of $\Delta t^*=0.8$, the MD time step still being $\delta t^*=0.0008$, and where each gauss point is again represented by a cube of side 14.1. Thus, in these two schemes we are not simulating each part of the larger system through a gauss point MD simulation, but are rather relying on linear interpolation of velocities between consecutive grid points to accurately represent regions which are not simulated. Comparisons with full-fledged MD simulations for the same systems have been shown in Fig. 4, and we clearly see that the scale bridging method does provide an accurate solution in these cases too, even in regions of space where the velocity profiles are varying significantly. These notions further reiterate that the proposed method can be used to truly access large macroscopic systems, an important goal of current simulation methods.

Regarding the net gain in computation time when the proposed method is used in a scale-bridging sense, the ratio of the computation time taken to simulate the rheology of the

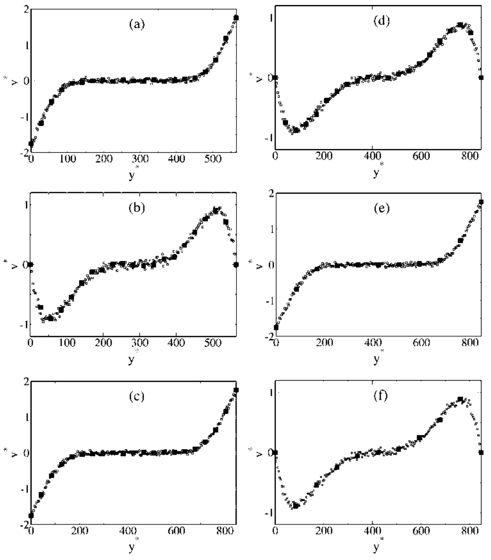

FIG. 4. Velocity profiles obtained for system thicknesses (a), (b) 564σ and (c)–(f) 846σ, employing (a)–(d) twenty and (e), (f) ten unit cells for the scale-bridging method. Within each plot the small hollow squares represent data obtained from direct MD and the filled squares represent that obtained using the scale-bridging scheme. For thickness$=564\sigma$ the plots are for times (a) $t^*=200$ and (b) $t^*=400$. For thickness$=846\sigma$ the plots are for times (c), (e) $t^*=400$ (d), (f) $t^*=800$.

given system by employing the proposed method to the computation time taken to perform a full-fledged simulation of the system is approximately given by the ratio of the total volume of all the MD cells at the different gauss points to the net volume of the whole system. This comes about from the fact that since linked list is used for the MD simulations, for the same number of time steps the computation time needed for the simulation is directly proportional to N, the number of monomers in the volume, for large N. Also, since the different gauss points interchange information only very occasionally, parallelization is very straightforward with the proposed method, whereby each MD simulation cell corresponding to a given gauss point is simulated by a different computer.

Our method, in spirit, is akin to the methods used by Laso and Ottinger [35] and Bell *et al.* [36], where they too use shear stresses that are calculated from molecular configurations during the simulation and combine it with continuum equations, thus obviating the need of even a history-dependent constitutive equation. Their models though, are of the mean-field type, in the sense that the evolution of the molecular configuration at a given point within the system does not explicitly depend on the configuration of the rest of the system. Hence, their models for the polymeric system itself are not as realistic as ours to begin with, and moreover, a full-fledged simulation of the whole system employing their models does not have a concrete meaning, and therefore within the realm of simulations they cannot propose any benchmark to verify the accuracy of their method.

Regarding the generalization of the method in two and three dimensions, we anticipate the need of finite-element methods in place of the finite difference that we have used till now for the continuum part of our proposed scheme. Also, for a more general shear-rate profile at a given point within the system, more generalized Lees-Edwards periodic boundary conditions will have to be implemented for the MD simulation cell. Also, in this paper, our method is implemented in such a way that both compressibility of the polymer melt and viscous generation of heat are neglected. Further work regarding how to incorporate these factors within the proposed scheme is in progress.

In summary, we have proposed a simulation method based on a scale-linking scheme for determining the mesoscale velocity evolution in fluid systems with large stress-relaxation times. In such systems the use of a steady-state constitutive equation of viscosity is expected not to produce the correct rheology. We demonstrated that velocity evolutions in such systems can be determined with great accuracy by comparing them with results obtained from direct full-fledged molecular dynamics simulations. The proposed method cannot only be used to conveniently parallelize large MD simulations, but can also be used in a scale bridging sense in that we need to only simulate small parts of the system through the MD method with the continuum approach providing an accurate means of interpolating between these points. This approach therefore provides considerable promise in the simulation of condensed phase systems in the limits of size which are relevant to macroscopic processing.

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[1] K. Esselink *et al.*, Phys. Rev. E **51**, 1560 (1995).

[2] L. D. J. C. Loyens *et al.*, Mol. Phys. **86**, 171 (1995).

[3] J. J. de Pablo (unpublished).

[4] X. B. Nie *et al.*, Phys. Fluids **16**, 3579 (2004).

[5] X. B. Nie *et al.*, J. Fluid Mech. **500**, 55 (2004).

[6] S. Sirisup *et al.*, J. Comput. Phys. **207**, 568 (2005).

[7] A. Armaou *et al.*, Comput. Chem. Eng. **29**, 731 (2005).

[8] R. Rico-Martinez *et al.*, J. Comput. Phys. **196**, 474 (2004).

[9] R. Delgado-Buscalioni and P. V. Coveney, Phys. Rev. E **67**, 046704 (2003).

[10] J. Fish and C. Schwob, Int. J. Multiscale Comp. Eng. **1**, 43 (2003).

[11] J. Fish and W. Chen, Int. J. Numer. Methods Eng. (2005) (to be published).

[12] J. Fish and Z. Yuan, Int. J. Numer. Methods Eng. (2005) (to be published).

[13] W. E. and B. Engquist, Commun. Math. Sci. **1**, 87 (2002).

[14] T. J. R. Hughes, Comput. Methods Appl. Mech. Eng. **127**, 387 (1995).

[15] R. E. Rudd and J. Q. Broughton, Phys. Rev. B **58**, R5893 (1998).

[16] T. Y. Hou and X. Yu, J. Comput. Phys. **134**, 169 (1997).

[17] I. G. Kevrekidis *et al.*, Commun. Math. Sci. **1**, 715 (2003).

[18] E. B. Tadmor *et al.*, Philos. Mag. A **73**, 1529 (1996).

[19] W. A. Curtin and R. E. Miller, Modell. Simul. Mater. Sci. Eng. **11**, 33 (2003).

[20] J. Fish, *Discrete-to-Continuum Scale Bridging, Book Chapter in Multiscaling in Molecular and Continuum Mechanics* (Springer, Berlin, 2006).

[21] J. Fish and Y. Tang, Int. J. Multiscale Comp. Eng. (to be published).

[22] I. G. Kevrekidis *et al.*, AIChE J. **50**, 1346 (2004).

[23] D. Xiu *et al.*, Comput. Sci. Eng. **7**, 16 (2005).

[24] R. Khare *et al.*, J. Chem. Phys. **107**, 2589 (1997).

[25] R. Khare *et al.*, J. Chem. Phys. **114**, 7593 (2001).

[26] S. Q. Chen *et al.*, Multiscale Model. Simul. **3**, 871 (2005).

[27] W. N. E. *et al.*, J. Am. Math. Soc. **18**, 121 (2005).

[28] M. Zhou, Proc. R. Soc. London, Ser. A **459**, 2347 (2003).

[29] W. Chen and J. Fish, Int. J. Numer. Methods Eng. (to be published).

[30] K. Kremer and G. Grest, J. Chem. Phys. **92**, 5057 (1990).

[31] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Non-Equilibrium Liquids* (Academic Press, London, 1990).

[32] S. Barsky and M. Robbins, Phys. Rev. E **65**, 021808 (2002).

[33] S. Sen *et al.*, Macromolecules **38**, 650 (2005).

[34] M. Kroger *et al.*, J. Rheol. **37**, 1057 (1993).

[35] M. Laso and H. C. Ottinger, J. Non-Newtonian Fluid Mech. **47**, 1 (1993).

[36] T. W. Bell *et al.*, Macromolecules **30**, 1806 (1997).