Multiscale Modeling of Polymer Rheology

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We propose a novel 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 these simulations 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 non-linear viscoelasticity of complex fluids.

An important goal for conventional computer methods, e.g., Monte Carlo and Molecular Dynamics, is to simulate large enough systems so as to approach the truly macroscopic limit where several interesting phenomena are thought to occur. 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. The simulation of large systems for long times thus remains a currently unachievable "holy grail" of research. Current methods designed to attain the goal of simulating large systems partition the computational effort between several computers: information between the different CPUs is then exchanged either through shared memory or through message passing [1–3]. The message passing method, which is obviously favorable when one wants to run programs across clusters of small computers, suffers from latency issues which underlie these communications. Such message passing has to be performed at each step emphasizing this difficulty. New methods to circumvent these difficulties perform full-fledged atomistic simulations for the part of the system with large property gradients, and use a continuum approach for the rest. The question lies in how the two parts would communicate, and one rich class of multiscale problems focuses on this very question [4–8].

Here we propose a novel 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 occassionally communicate between these MD simulations through the use of a continuum method, without using a constitutive model in this description. 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 non-linear flow situations, involving memory effects, where methods employing constitutive models may be expected to be inadequate.

The schematic representation of the fine scale and the coarse scale problems and the proposed scale bridging idea is sketched schematically in Figure 1. We adopt the Lagrangian framework since we desire to incorporate memory effects, and the consequent dependence of properties on the overall deformation. Following the Generalized Mathematical Homogenization (GHM) theory, the governing equations for the fine scale problem, the scale bridging equation and the coarse grained problem are:

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

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.

In the following we describe our proposed method in the context of a specific problem. Consider the continuum equation describing a polymer melt, which is undergoing one dimensional oscillatory shear flow [Figure 1]. As sketched in Figure 1, we consider finite difference discretization in the y direction using $(N+1)$ grid points. The continuum problem then can be solved by an appropriate discretization of the coarse grained problem in Eq. 1:

$$
\rho \frac{v_x(i, t+\Delta t) - v_x(i,t)}{\Delta t} = \frac{\sigma_{xy}(j+1) - \sigma_{xy}(j)}{\Delta y} \tag{2}
$$

where $\sigma_{xy}(j)$ is the macroscopic modified virial stress in the xy plane at the gauss point j which is positioned in the middle of the interval between the grid points i and $i-1$ in the continuum framework. The continuum equations yield velocity profiles which are fed into the gauss point MD simulations. These MD simulations yield the micrscopic stresses which are fed back to the continuum solver, thus allowing us to simulate truly large systems.

Since the finite difference method considers a linearly varying velocity profile between grid points, a fact that is consistent with the Lees-Edwards periodic boundary conditions used to simulate shear flow in a MD simulation [9], each gauss point actually corresponds to a MD simulation whose y size is $1/N$ as large as the overall system size. In this process we have therefore broken up the large macroscopic system into a series of smaller systems, each of which independently has three dimensional periodic boundary conditions imposed on them. The message passing between these different parts of the large system are achieved through the use of Eq. 1. The continuum (Cauchy) stress at each gauss point corresponding to a unit cell positioned at $\mathbf{x}_\xi$ is computed using the modified virial theorem as suggested in

[10, 11]. At each time t, Eq. 1 yields a solution for the velocity profile in the macroscopic system. We conduct *independent* MD simulations at each gauss point for the a time interval Δt corresponding to the time step of the macro problem integrator. The mean value of the transient stress in each gauss point then allows us to update velocities, and thus evolve the system. Note that the the coarse scale problem is thus modeled using constitutive law-free continuum equations, and that the fine scale problem at a gauss point in the coarse scale is represented using molecular dynamics equations.

We therefore propose that this multiscale simulation method, which involves bidirectional message passing between the small system and the "macroscopic" system of interest allows us a new means of simulating large systems without frequent message passing [1, 2, 4–8, 12–29]. 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, bi-directional information passing schemes.

Large System Simulations: The large system whose behavior we want to model by the proposed scale bridging method corresponds to a box of size 14.1σ on a side in the x and z directions, while the y direction is 282σ. To generate reference data against which the proposed method can be calibrated we have conducted Molecular Dynamics simulations on a polymer melt in this box under the action of an oscillatory, one dimensional shear flow.

Polymer chains are modeled in the framework of the pioneering ideas of Kremer and Grest: each chain is comprised of beads connected by FENE springs [30]. All beads interact with a shifted, purely repulsive Lennard-Jones potential $U_{\rm LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon$ for $r < 2^{1/6}\sigma$ and $U_{\rm LJ}(r) = 0$ for $r > 2^{1/6}\sigma$. All quantities reported from now on are reduced in terms of σ for length, $\tau = \sigma\sqrt{(}m/\epsilon)$ for time and the monomer mass m for mass respectively, and denoted by a $(*)$ in the superscript . We model chains of length 120 each, at an overall 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 are $v^* = \pm 2.23\sin(\omega t^*)$ 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. The system was simulated through the standard Molecular Dynamics simulation method with a profile unbiased y-z thermostat [9, 31]. At the end of every MD time step only the y and the z components of particle velocities are re-scaled according to the given temperature. The integration was performed at a constant temperature of $T_0^* = (k_B T_0/\epsilon) = 1$ and a time step of $\delta t^* = 0.0008$.

Scale Briding Simulations: In the proposed method each gauss point was represented by a cube of size 14.1. The velocities at the boundaries of each box were generated by the solution of the continuum equations. A standard Lees-Edwards boundary condition was used to simulate these boxes. We employed the uniform profile-biased thermostat [9] where we assume a linear coarse velocity profile consistent with the instantaneous shear-rate imposed on the cell and rescale all three components of particle velocities after every MD time step. The starting configurations for each of these gauss points correspond to the ending configuration of the previous simulation, which had been used by the continuum model to generate the current velocity profile. To improve the accuracy of the simulations we have used multiple independent realizations of the gauss points so as to obtain better estimates of the transient stress, σ_i. 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, these second class of simulations provide a poor agreement between the proposed scale bridging method and the full scale MD simulation.

Both the fine and coarse scale systems are typically integrated using explicit methods. In this specific problem we integrate the coarse scale problem using the finite difference scheme of Eq. 2. The integration time steps were δt, for the gauss point, and Δt , for the coarse scale problem, with $\delta t << \Delta t$. The time step δt chosen for the molecular dynamics has to satisfy $\delta t << \tau$,where τ, already defined, represents the smallest time scale in the system. Δt also has to much smaller than any characteristic time corresponding to the dynamic boundary conditions imposed on the system boundary, i.e., $\Delta t << T = 2\pi/\omega$ where T is the time period of oscillation. We again choose $\delta t^* = 0.0008$. Within every unit cell used in our multiscale scheme, non-equilibrium molecular dynamics simulation is carried out following the fifth-order predictor-corrector algorithm [9] using the Lees-Edward periodic boundary condition and employing the linear profile-biased thermostat [9] where

the velocity re-scaling is done after every MD time step.

Figures 2 compare the results of the velocity profile across the simulation box as obtained from the full MD simulations as well as the multiscale method employing a coarse time step of $\Delta t^* = 0.08$. 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 [32] 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. A direct consequence of this statement is that our method is thus capable of simulating even larger systems, simply by assigning more computers to handle an even larger number of grid points. However, the real bound on this algorithm is the time scales that can be accessed. Since memory effects are important the coarse grain time steps, Δt, must be commensurate with the length of the gauss point MD simulations. Thus, no advantage is obtained in accessing truly long time scales by this approach.

Another fact which further stresses the advantages of the proposed work is discussed here. Following the early work of Kroger and Hess we know that this polymeric fluids are shear thinning. Since we know 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. Eq. 1 can then be solved without resort to the grid point simulations. Figures 2 clearly show 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 within each unit cell in the multiscale method and in the case of steady shear 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 only employ 20 equidistant gauss points, and even as few as 10 gauss points for the larger system, using a coarse time step of $\Delta t^* = 0.8$, where each gauss point is again represented by a cube of side 14.1. Thus, in these two new schemes we are not simulating each part of the larger system through a gauss point MD simulation, but are rather relying on the applicability of Eq. 1 to accurately represent regions which are not simulated. Figures 4 clearly show that the scale bridging method does provide an accurate solution even in these cases, 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.

In summary, we have proposed a simulation method based on a scale-linking scheme for determining the meso-scale velocity evolution in fluid systems with large stress-relaxation times. In such systems the use of a steady state consitutive 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 can not 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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Figure captions:

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 method yield a velocity profile which are used in the next set of MD simulations.

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.

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=564σ the plots are for times (a) $t^* = 200$ and (b) $t^* = 400$. For thickness=846σ are plots are for times (c,e) $t^* = 400$ (d,f) $t^* = 800$.

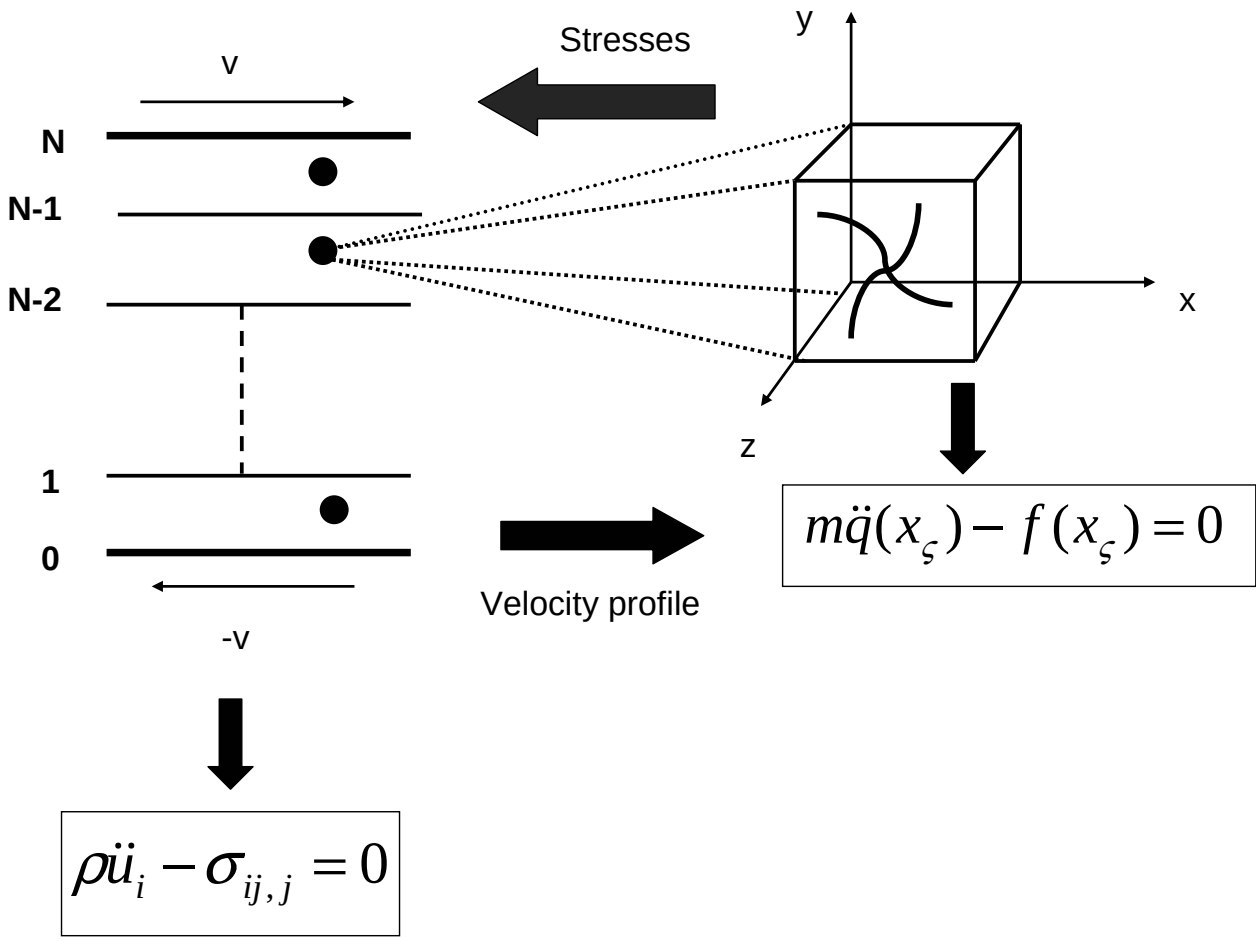
v
N
N-1
N-2
1
0
-v
Stresses
y
x
z
Velocity profile
$m\ddot{q}(x_\varsigma) - f(x_\varsigma) = 0$
$\rho\ddot{u}_i - \sigma_{ij,j} = 0$

FIG. 1:

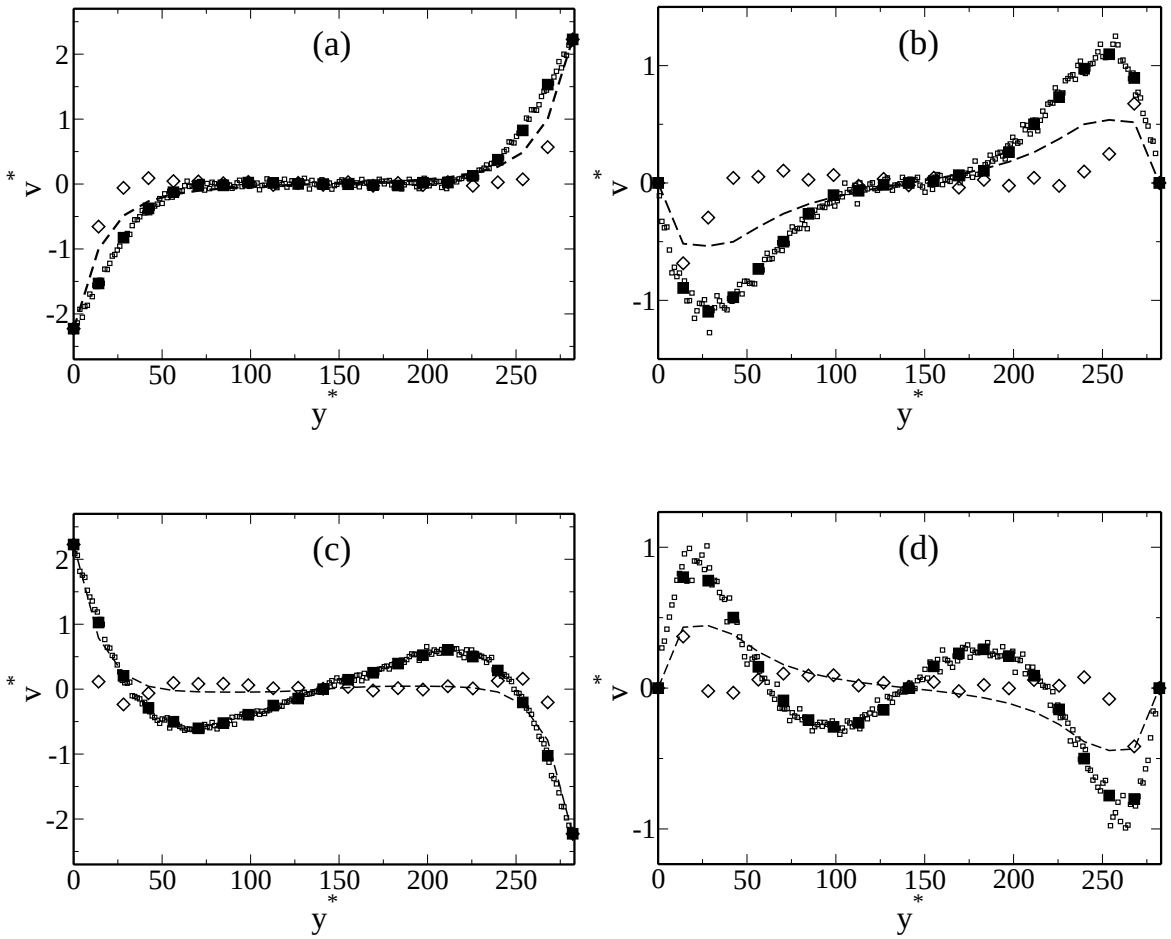

FIG. 2:

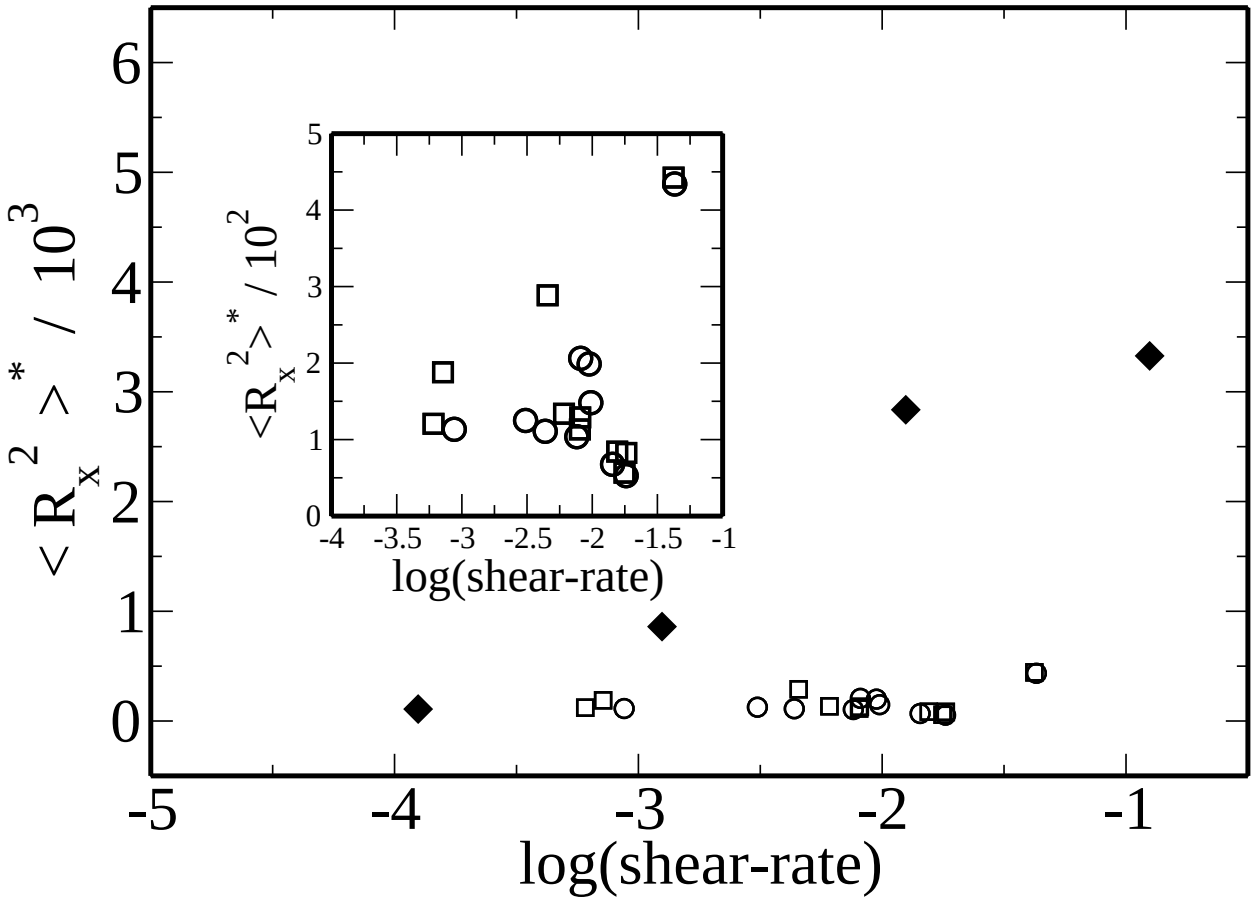

FIG. 3:

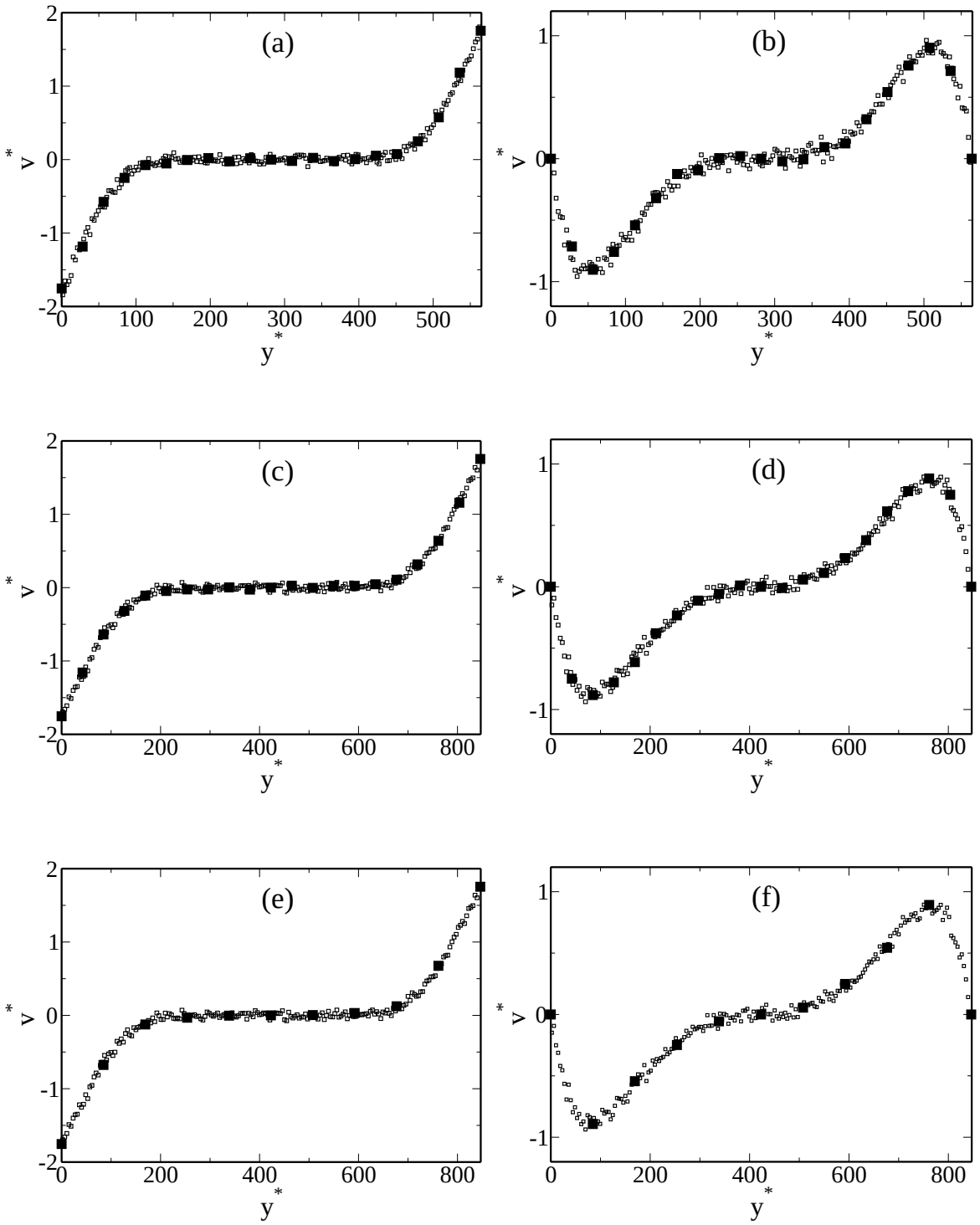

FIG. 4: