Multiscale Rheology: New Results for the Kinetic Scale

B. Kallemov*, G. H. Miller*, S. Mitran**, and D. Trebotich***

* University of California, Davis, CA, USA, {bkkallemov,grgmiller}@ucdavis.edu
** University of North Carolina, Chappel Hill, NC, USA, mitran@unc.edu
*** Lawrence Berkeley National Laboratory, Berkeley, CA, USA, treb@lbl.gov

ABSTRACT

We present several new results on the kinetic, i.e., mesoscale, level of a continuum–kinetic–microscopic approach to multiscale modeling of complex fluids. We choose the microscopic level as Kramers' bead-rod model for polymers, which we describe as a system of stochastic differential equations with an implicit constraint formulation. The associated Fokker-Planck equation is then derived, and adiabatic elimination removes the fast momentum coordinates. Approached in this way, a comparatively simple result is obtained consisting of drift but no diffusion terms. We demonstrate computation of viscoelastic stress divergence using this multiscale approach.

Keywords: viscoelasticity, complex fluids, multiscale, microfluidics

1 INTRODUCTION

Complex fluids are characterized by microscopic constituents whose internal configuration influences momentum transfer observed at a macroscopic scale in which the fluid can be considered a continuum. The flow of an incompressible viscoelastic fluid at macroscopic length scales is given by the momentum equation

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} + \frac{1}{\rho} \nabla P = \nu \Delta \mathbf{u} + \frac{1}{\rho} \nabla \cdot \boldsymbol{\tau}, \tag{1}$$

together with the conservation of mass for an incompressible fluid

$$\nabla \cdot \mathbf{u} = 0. \tag{2}$$

In this formulation, $\rho\nu\Delta\mathbf{u}$ is the divergence of a viscous (Newtonian) stress tensor, which depends linearly on the fluid velocity gradients. This term alone accounts for the rheology of many simple fluids. But, when polymers are suspended in the fluid they contribute an extra stress $\boldsymbol{\tau}$ to the system. To simulate a system like (1,2) a closure is needed to relate the viscoelastic stress to the fluid velocity, $\boldsymbol{\tau}(\mathbf{x}, t, \mathbf{u})$. A variety of macroscopic constitutive closure relations have been proposed to approximate at the continuum level the dynamics associated with the molecular scale, among which we consider the class of relations in partial differential equation (PDE) form. For instance, the Oldroyd-B PDE describes a dilute (non-interacting) suspension of infinitely-extensible springs connected to point masses which interact with the fluid by Stokes drag. Despite the great simplicity of this model, it adequately represents the constitutive behavior of a class of fluids (Boger fluids) under restricted flow regimes. The approximation of a polymer by a spring is motivated by the statistical mechanics result that a freely-jointed polymer obeys length distribution statistics that are approximately Gaussian: a long polymer is approximately a spring, and the motive force is entropic. In flows with large shears, the Oldroyd-B model overestimates the extension of the polymers, which is finite for a physical polymer but unbounded in the entropic spring approximation. A compensating force can be added to the constitutive model to prevent overextension, resulting in the FENE-P model. Models of greater complexity have been proposed to correct limitations of these simple constitutive closures, but there are limits to the ability of a macroscopic constitutive model to approximate the dynamics associated with the large number of degrees of freedom contained in even simple models of a linear polymer.

This motivates a multiscale approach, where the extra stress $\boldsymbol{\tau}$ will be obtained somehow from a molecular scale model, and provided as a source term to a numerical method for (1,2). A pioneering approach along these lines is the CONNFFESSIT method [7] which represents dumbbell polymers as a system of stochastic differential equations (SDE). A drawback of the approach is the enormous number of SDEs that must be solved for even a simple system. Mitran [9] introduced two ideas that improve the performance of such multiscale models: the association of a kinetic scale between the continuum and molecular and levels, and the use of time parallelism to make a very fast implementation using graphical processing units.

In prior work [2], [5] we developed new high-order numerical methods for the simulation of a Kramers bead-rod freely-jointed polymer. That is, a set of N "beads," point masses subject to Stokes drag and Brownian motion, connected by $N-1$ "rods," massless objects meant to keep the beads at constant relative separation. "Freely-jointed" means the rods can interpenetrate. A single polymer is given by the following system of constrained

SDEs:

$$\frac{\partial \mathbf{x}_i}{\partial t} = \mathbf{v}_i \tag{3a}$$

$$\frac{\partial \mathbf{v}_i}{\partial t} = \gamma(\mathbf{u}(\mathbf{x}_i, t) - \mathbf{v}_i) + \sigma \boldsymbol{\xi}_i \tag{3b}$$

$$\|\mathbf{x}_{i+1} - \mathbf{x}_i\| = a. \tag{3c}$$

Here, $\boldsymbol{\xi}_i$ is a vector of uncorrelated white noises associated with bead i, and a is the inter-bead spacing, commonly associated with the polymer Kuhn length. The parameter σ is given by

$$\sigma = \sqrt{\frac{2\gamma k_B T}{m}} \tag{4}$$

where m is the mass of a bead. The drag term $\gamma(\mathbf{u} - \mathbf{v})$ provides a coupling of the macroscopic flow to the microscale simulation. By itself, this model can calculate a number of classical results including the mean end-to-end distance in relaxed flow, velocity correlations along the chain.

We have also developed numerical schemes for coupling individual polymers with microfluidic flows [11], [3], [4]. This work, like CONNFFESSIT, couples directly the continuum and microscale dynamics.

Here, we present progress toward a continuum–kinetic–molecular multiscale model for dilute freely-jointed polymers in a Newtonian solvent. Kramers' freely-jointed model has finite extensibility and possesses a spectrum of relaxation times which differ by as much as N^2 for an N-bead polymer. Thus, while still highly idealized, it nonetheless possesses significant complexity and many more degrees of freedom than any practical macroscopic closure approximation. The emphasis here will be on the kinetic (mesoscale) layer of the multiscale scheme. We present new algorithms for the calculation and time propagation of this description, and show preliminary results.

2 THE KINETIC APPROXIMATION

Associated with the constrained SDEs (3) is a Fokker-Plank equation for the probability density function (PDF) $\Psi(\mathbf{q}, t)$, where $\mathbf{q} = \{\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N\}$ are the microscale configuration coordinates. If one could model Ψ, then one could generate (sample) representative polymer configurations. For example, if Ψ could be evaluated but has no special form, sampling could occur with Monte Carlo rejection sampling. If Ψ is known as a Gaussian mixture model it can be sampled more efficiently. The ability to efficiently generate samples $\mathbf{q}$, then compute the fluid stress associated with these samples by microscale simulation, is one of the efficiencies of Mitran's approach. The information associated with millions of microscale SDEs does not need to be stored: they can be sampled and discarded if the kinetic PDF is known.

To obtain the Fokker-Plank equation associated with (3) we first rewrite the system without constraints. This can be accomplished by incorporating the constraints as Lagrange multipliers, with value given by an implicit function [8], [5]. The result can be written in block partitioned form

$$d\mathbf{p} = \mathbf{f}dt + \mathbf{g}d\mathbf{W} \tag{5}$$

$$\mathbf{p} = \left(\frac{\mathbf{q}}{\dot{\mathbf{q}}}\right) \tag{6}$$

$$\mathbf{f} = \left(\frac{\dot{\mathbf{q}}}{\mathbf{F}}\right) \tag{7}$$

$$\mathbf{g} = \left(\frac{\mathbf{0}}{\boldsymbol{\Gamma}}\right) \tag{8}$$

where

$$\begin{gathered}\mathbf{F}_i = \gamma(\mathbf{u}(\mathbf{x}_i) - \mathbf{v}_i) + \left[(\Delta_{i-1}\mathbf{x})\mathbf{A}^{-1}_{i-1,j} - (\Delta_i\mathbf{x})\mathbf{A}^{-1}_{i,j}\right] \times \\ \left[(\Delta_j\mathbf{x}) \cdot \gamma(\Delta_j\mathbf{u} - \Delta_j\mathbf{v}) + (\Delta_j\mathbf{v}) \cdot (\Delta_j\mathbf{v})\right]\end{gathered} \tag{9}$$

and

$$\begin{gathered}\boldsymbol{\Gamma}_i = \sigma\Big\{\left[(\Delta_{i-1}\mathbf{x})\mathbf{A}^{-1}_{i-1,j-1} - (\Delta_i\mathbf{x})\mathbf{A}^{-1}_{i,j-1}\right](\Delta_{j-1}\mathbf{x})^T - \\ \left[(\Delta_{i-1}\mathbf{x})\mathbf{A}^{-1}_{i-1,j} - (\Delta_i\mathbf{x})\mathbf{A}^{-1}_{i,j}\right](\Delta_j\mathbf{x})^T + \mathbf{I}\delta_{ij}\Big\}.\end{gathered} \tag{10}$$

In these expressions, $d\mathbf{W}$ is a vector of DN independent Wiener derivatives in D dimensions, and $\mathbf{A}$ is the $(N-1) \times (N-1)$ tridiagonal matrix:

$$\mathbf{A}_{ij} = \begin{cases} -2(\Delta_i\mathbf{x}) \cdot (\Delta_i\mathbf{x}) & \text{if } i = j \\ (\Delta_i\mathbf{x}) \cdot (\Delta_j\mathbf{x}) & \text{if } |i-j| = 1 \\ 0 & \text{otherwise.} \end{cases} \tag{11}$$

$\Delta_i\mathbf{x}$ is shorthand for $\mathbf{x}_{i+1} - \mathbf{x}_i$, etc., and such terms are understood to be zero if $i < 1$ or $i \geq N$.

Note that we have included momentum in our SDEs, which implies the applicability of Itô calculus. It is not uncommon for momentum to be ignored (e.g., [8]) which then necessitates Stratonovich calculus. See also [6]. We will find that including momentum at this point leads to a simple form for the PDF because of the zero block in $\mathbf{g}$ (8).

It follows from (5) and the rules of Itô differentiation that for any measurable function $s(\mathbf{p})$ there exists the SDE

$$ds = \left[\mathbf{f} \cdot \nabla_{\mathbf{p}} s + \frac{1}{2}(\mathbf{g}\mathbf{g}^T) : \nabla_{\mathbf{p}}\nabla_{\mathbf{p}} s\right] dt + (\mathbf{g} \cdot \nabla_{\mathbf{p}} s) d\mathbf{W}, \tag{12}$$

and so in expectation

$$d\langle s\rangle = \left\langle \mathbf{f} \cdot \nabla_{\mathbf{p}} s + \frac{1}{2}(\mathbf{g}\mathbf{g}^T) : \nabla_{\mathbf{p}}\nabla_{\mathbf{p}} s \right\rangle dt. \tag{13}$$

But, given the PDF, one also has

$$\langle s \rangle = \int d\mathbf{p} \Psi(\mathbf{p}) s(\mathbf{p}) \tag{14}$$

so

$$\begin{aligned} \frac{d\langle s \rangle}{dt} &= \int d\mathbf{p} \frac{\partial \Psi(\mathbf{p})}{\partial t} s(\mathbf{p}) \\ &= \int d\mathbf{p} \Psi(\mathbf{p}) \left(\mathbf{f} \cdot \nabla_{\mathbf{p}} s + \frac{1}{2} (\mathbf{g}\mathbf{g}^T) : \nabla_{\mathbf{p}} \nabla_{\mathbf{p}} s \right). \end{aligned} \tag{15}$$

Integrate this expression with respect to time, then twice by parts with Ψ and $\nabla\Psi$ zero at infinity. The result is

$$\begin{aligned} 0 = \int dt \int d\mathbf{p}\ s \Bigg(&\frac{\partial \Psi}{\partial t} + \nabla_{\mathbf{p}} \cdot (\mathbf{f}\Psi) - \\ &\nabla_{\mathbf{p}(i)} \nabla_{\mathbf{p}(j)} \left(\frac{1}{2} (\mathbf{g}\mathbf{g}^T)_{ij} \Psi \right) \Bigg) \end{aligned} \tag{16}$$

giving the Fokker-Planck equation

$$\frac{\partial \Psi}{\partial t} + \nabla_{\mathbf{p}} \cdot (\mathbf{f}\Psi) - \nabla_{\mathbf{p}(i)} \nabla_{\mathbf{p}(j)} \left(\frac{1}{2} (\mathbf{g}\mathbf{g}^T)_{ij} \Psi \right) = 0 \tag{17}$$

in the space of coordinates and particle velocity, and containing both drift and diffusion contributions. Substituting the block partitions of $\mathbf{f}$ (7) and $\mathbf{g}$ (8), it is apparent that the diffusion term is only associated with the velocity coordinates:

$$\frac{\partial \Psi}{\partial t} = -\dot{\mathbf{q}} \cdot \nabla_{\mathbf{q}} \Psi - \nabla_{\dot{\mathbf{q}}} \cdot (\mathbf{F}\Psi) + \frac{1}{2} \mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk} \frac{\partial^2 \Psi}{\partial \dot{\mathbf{q}}_i \dot{\mathbf{q}}_j} \tag{18}$$

where $\mathbf{\Gamma}$ depends on $\mathbf{q}$ but not $\dot{\mathbf{q}}$.

At this point we note that the momentum coordinates evolve rapidly relative to the position coordinates, because of the magnitude of γ. We use adiabatic elimination to remove these fast modes from the Fokker-Planck equation [10]. For the stationary state of the fast (momentum) mode we have

$$\frac{\partial}{\partial \mathbf{v}_i} \cdot \left[-\mathbf{F}_i + \frac{1}{2} \mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk} \frac{\partial}{\partial \mathbf{v}_j} \right] \psi = 0. \tag{19}$$

We assume that this holds for each i, so that summation is not required. This assumption is motivated by the fact that velocity is very nearly δ-correlated along a polymer chain [1], [5]. With this assumption,

$$-\mathbf{F}_i \psi + \frac{1}{2} \mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk} \frac{\partial}{\partial \mathbf{v}_j} \psi = \mathbf{c}_i \tag{20}$$

for some vector $\mathbf{c}_i$ that is independent of $\mathbf{v}_i$. Now integrate (20) with respect to velocity over the entire velocity space $[-\infty, +\infty]^{DN}$:

$$\int d\mathbf{v} \mathbf{c}_i = -\langle \mathbf{F}_i \rangle + \frac{1}{2} \mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk} \int d\mathbf{v} \nabla_{\mathbf{v}_j} \psi. \tag{21}$$

The integral on the right hand side must be zero since ψ and its gradient must be zero at infinity. Then, if expectation $\langle \mathbf{F}_i \rangle$ is bounded, it follows that the integral on the left hand side must be bounded: $\mathbf{c}_i = 0$ and therefore $\langle \mathbf{F}_i \rangle = 0$.

This convenient result is not unexpected. $\mathbf{F}_i$ is the smooth part of the acceleration experienced by bead i, $\gamma(\mathbf{u}_i - \mathbf{v}_i)$, projected onto the space of accelerations that satisfy the second derivative of the holonomic constraint (3c). That $\langle \mathbf{F}_i \rangle = 0$ then signifies that subject to constraints, $\langle \mathbf{v}_i \rangle = \mathbf{u}_i$, which is the behavior anticipated in the limit $\gamma \to \infty$ that motivates dropping momentum in the first place.

With $\mathbf{c}_i = 0$, integration of (20) is straightforward,

$$\psi \propto \exp \left(2 \mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk} \int d\mathbf{v'}_j^T \mathbf{F}_i \right). \tag{22}$$

With this fast mode determined, the Fokker-Planck dynamics (19) reduce to

$$\frac{\partial \Psi}{\partial t} = \bar{\mathbf{v}} \cdot \nabla_{\mathbf{x}} \Psi \tag{23}$$

with

$$\bar{\mathbf{v}} = \int^{\dagger} d\mathbf{v}\ \mathbf{v} \psi \tag{24}$$

the vector of average velocities. The dagger signifies that the integral is over the space of velocities consistent with the constraint. A more formal derivation would use internal coordinates, but we find that obscures the essential result.

It can be shown that

$$\bar{\mathbf{v}} = \frac{\int d\mathbf{v} \mathbf{v} \exp \left(2 \mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk} \int d\mathbf{v'}_j^T \mathbf{F}_i \right)}{\int d\mathbf{v} \exp \left(2 \mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk} \int d\mathbf{v'}_j^T \mathbf{F}_i \right)} \tag{25}$$

is normally distributed with mean $\mathbf{u}(\mathbf{x})$ and variance $k_B T/m$. This is shown by considering velocities on the velocity constraint manifold. The projection of arbitrary velocities $\mathbf{v}'$ onto the constraint manifold is (see [5])

$$\begin{aligned} \mathbf{v}_i &= \mathbf{v}'_i + \left[(\Delta_{i-1}\mathbf{x}) \mathbf{A}^{-1}_{i-1,j} - (\Delta_i \mathbf{x}) \mathbf{A}^{-1}_{i,j} \right] (\Delta_j \mathbf{x}) \cdot (\Delta_j \mathbf{v}'_\beta) \\ &= \frac{1}{\sigma} \Gamma_{ik} \mathbf{v}'_k. \end{aligned} \tag{26}$$

Therefore, subject to the restriction that all velocities in (25) are on the constraint manifold,

$$\mathbf{\Gamma}\mathbf{\Gamma}^T = \sigma^{-2} \mathbf{I} = \frac{m}{2\gamma k_B T} \mathbf{I}. \tag{27}$$

Then, with $\mathbf{F}$ the projection of the smooth acceleration,

$$2(\mathbf{\Gamma}_{ik} \mathbf{\Gamma}_{jk})^{-1} \int d\mathbf{v'}_j^T \mathbf{F}_i = -\frac{m}{2k_B T} (\mathbf{u} - \mathbf{v})_i^T (\mathbf{u} - \mathbf{v})_j, \tag{28}$$

and so it follows that (25) is normally distributed with mean $\mathbf{u}$ and variance k_BT/m.

Result (23) has a trivial solution,

$$\Psi(\mathbf{x},\ t+\Delta t) = \Psi(\mathbf{x} - \bar{\mathbf{v}}\Delta t,\ t): \tag{29}$$

the PDF is advected with velocity $\bar{\mathbf{v}} \sim \mathbf{u}$.

For the solution, we propose the following two stage process. First, one advects the PDF using the center-of-mass velocity, $\mathbf{u}_{\text{com}}$:

$$\Psi_{\text{adv}}(x,\ t+\Delta t) = \Psi(\mathbf{x} - \mathbf{u}_{\text{com}}\Delta t,\ t). \tag{30}$$

Next, account for the variation of fluid velocity along the polymer chain, and the variation in velocity associated with the distribution (25):

$$\Psi(\mathbf{x},\ t+\Delta t) \approx \Psi_{\text{adv}}(\mathbb{P}_{\mathbf{x}}(\mathbf{x} - \Delta t\delta\mathbf{u}),\ t+\Delta t) \tag{31}$$

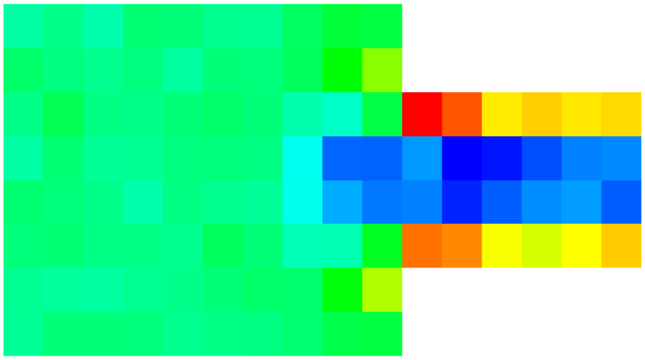
where

$$\delta\mathbf{u}_i = (\mathbf{x}_i - \mathbf{x}_{\text{com}}) \cdot \nabla\mathbf{u} + \vec{\mathbb{N}}(0,1)\sqrt{k_BT/m} \tag{32}$$

is the velocity perturbation associated with bead i, $\vec{\mathbb{N}}(0,1)$ is a vector of Gaussian normal deviates with mean 0 and variance 1, and $\delta\mathbf{u}$ is the vector comprised of all $\delta\mathbf{u}_i$. $\mathbb{P}_x$ is the projection onto the constraint (3c).

By means of this algorithm, one has two methods for computing Ψ in Mitran's continuum–kinetic–molecular framework: (i) advect it as described above, or (ii) generate an ensemble of polymers at t, march these forward in time to $t+\Delta t$ with the algorithm of [5], then find the PDF at $t+\Delta t$ that models the updated molecular configuration. Together these can be applied in a predictor-corrector manner, with the microscopically-derived PDF being the more trustworthy.

Figure 1: stress gradient, x component, for a 2:1 contraction with $Re \approx 1$.



ACKNOWLEDGEMENTS

B. Kallemov was supported by the Bolashak scholarship of the President of the Republic of Kazakhastan. G.H. Miller, S. Mitran, and D. Trebotich were supported by the U.S. Department of Energy Office of Advanced Scientific Computing Research under grants DE-SC0001981 and A10-0486-001, and contract DE-AC02-05-CH11231, respectively.

REFERENCES

[1] S.F. Edwards and A.G. Goodyear, "The velocity distribution function for a polymer chain," J. Phys. A Gen. Phys., 5, 1188-1195, 1972.

[2] B. Kallemov, G.H. Miller, and D. Trebotich, "A Duhamel approach for the Langevin equations with holonomic constraints," Molecular Simulation, 35, 440–447, 2009.

[3] B. Kallemov, G.H. Miller, and D. Trebotich, "Numerical simulation of polymer flow in microfluidic devices," Proc. Fourth SIAM Conference on Mathematics for Industry, pp. 93–98, 2010.

[4] B. Kallemov, G.H. Miller, and D. Trebotich, "A higher-order accurate fluid-particle algorithm for polymer flows," Molecular Simulation, in press (available online, DOI: 10.1080//08927022.2010.543977).

[5] B. Kallemov and G.H. Miller, "A second-order strong method for the Langevin equations with holonomic constraints," SIAM J. Sci. Comput., 33, 653–676, 2011.

[6] R. Kupferman, G.A. Pavliotis, and A.M. Stuart, "Itô versus Stratonovich white-noise limits for systems with inertia and colored multiplicative noise," Phys. Rev. E, 70, 036120, 2004.

[7] M. Laso and H.C. Öttinger, "Calculation of viscoelastic flow using molecular models: the CONNFFESSIT approach," J. Comput. Phys. 47, 1-20, 1993.

[8] T.W. Liu, "Flexible polymer chain dynamics and rheological properties in steady flows," J. Chem. Phys., 90, 5826–5842, 1989.

[9] S. Mitran, "Time parallel kinetic-molecular interaction algorithm for CPU/GPU computers," Proc. Comp. Sci., 1, 745–752, 2010.

[10] H. Risken, *The Fokker Planck Equation*, Springer-Verlag, 2nd edition, 1989.

[11] D. Trebotich, G.H. Miller, P. Colella, D.T. Graves, D.F. Martin, and P.O. Schwartz, "A tightly coupled particle–fluid model for DNA-laden flows in complex microscale geometries," in *Computational Fluid and Solid Mechanics 2005*, K.J. Bathe editor, Elsevier, pp. 1018-1022, 2005.