Hydrodynamics of Semidilute Polymer Solutions

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Hydrodynamic equations for semidilute polymer-solvent solutions are derived for both Rouse and reptation dynamics, with emphasis on the coupling between concentration fluctuations and polymer elastic stress. For the Rouse model, we project microscopic Fokker-Planck equations down to the hydrodynamic variables plus a long-lived strain variable. Also, we construct a more general two-fluid model of polymer plus solvent which shows how elastic stresses may cause diffusion currents. One important consequence of this Letter is the extension of work by Helfand and Fredrickson on Rouse solutions in weak shear to the more relevant entangled case.

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There has been considerable interest for some time in the effect of shear flow on the concentration of polymer in semidilute solutions near phase separation.[1] In simple binary fluid mixtures[2,3] and two-component polymer melts[4] and solutions,[5] shear flow in the single-phase region suppresses concentration fluctuations and phase separation. In contrast, shear flow applied to entangled polymer-solvent mixtures leads to large *increases* in scattering, with extreme sensitivity to shear near the phase boundary.[1,5,6] Whether or not this enhanced scattering is indicative of a shifted phase boundary induced by shear is controversial.

Two recent Letters proposed dynamical theories of polymer solutions in the presence of flow; these two theories each attempt to compute the steady-state structure factor $S(q,\dot{\gamma})$ in the presence of simple shear flow, and thereby find the origin of the enhanced scattering. The papers took different approaches, and made markedly different predictions.

Helfand and Fredrickson[7] (HF) derived hydrodynamic equations from the Rouse model of microscopic chain dynamics,[8]

$$\zeta\left[\frac{\partial R(s)}{\partial t}-v(R(s))\right]=-\frac{\delta F_R}{\delta R(s)}+\theta$$
$$=3T\frac{\partial^2 R}{\partial s^2}-\nabla\frac{\delta F_R}{\delta\phi}(R(s))+\theta. \tag{1}$$

Here, $R(s)$ is a chain configuration, $v(R)$ is the solvent velocity field, ζ is the monomer drag coefficient, and ϕ is the monomer concentration. F_R is the Rouse effective Hamiltonian

$$F_R=\int dV f(\phi)+\tfrac{3}{2}T\int ds\left(\frac{\partial R}{\partial s}\right)^2, \tag{2}$$

and θ is a Langevin noise source.

The Rouse model ignores both entanglements and hydrodynamic interactions (and is thus valid only near the overlap concentration ϕ^*). The concentration equation was derived by applying

$$\partial\phi/\partial t=\int ds[\delta\phi/\delta R(s)]\partial R(s)/\partial t$$

to the microscopic expression for the concentration, $\phi(x)=\int ds\,\delta(x-R(s))$. The result HF obtained is

$$\frac{\partial\phi}{\partial t}+\nabla\cdot v\phi-\zeta^{-1}\nabla\cdot\left(\phi\nabla\frac{\delta F_R}{\delta\phi}\right)+\zeta^{-1}\nabla\nabla:\Pi^{(e)}=\Theta. \tag{3}$$

(Here Θ is a new noise source appropriate for concentration fluctuations.) The elastic stress tensor $\Pi^{(e)}$ for flexible polymers is given quite generally[9] by

$$\Pi_{ij}^{(e)}=3T\int ds\,\delta(x-R(s))\frac{\partial R_i(s)}{\partial s}\frac{\partial R_j(s)}{\partial s}. \tag{4}$$

To Eq. (3) HF added the Navier-Stokes equation for the momentum density, and the "second-order fluid" constitutive equation for viscoelastic stress in a polymer solution under steady flow.

The $S(q)$ obtained by HF for low shear rates shows enhanced scattering with effects starting at $O(\dot{\gamma})$, but no shift in the critical temperature T_c (i.e., no change in the correlation length of fluctuations with wave vector normal to the flow).

Onuki[10] produced a phenomenological theory, which could be applied to polymer solutions obeying either Rouse or reptation dynamics. He introduced a new long-lived state variable W_{ij} corresponding to anisotropy of the distribution of chain bond directions (and thus to distortion of polymer coils). Next, a phenomenological free energy was introduced,

$$F_O=F_0+F_{\mathrm{el}}=\int dV f(\phi)+\tfrac{1}{4}\int dV E(\phi)\,\mathrm{tr}W^2, \tag{5}$$

with the second term corresponding to the elastic energy of the distorted coils. This would imply that the monomer chemical potential $\mu=\delta F_O/\delta\phi=\mu_0+\mu_{\mathrm{el}}$ is a function of the local state of stretch of the chains, which leads to striking predictions; for instance, chains would tend to migrate to the center of a Poiseuille flow.

Finally, Ref. 10 proposed hydrodynamic equations for the elastic distortion, polymer concentration, and momentum density in the form of Langevin equations. The most important difference[11] from HF is the concentration equation in Ref. 10,

$$\frac{\partial\phi}{\partial t}+\nabla\cdot v\phi-\lambda\nabla^2\left(\frac{\delta F_O}{\delta\phi}+\frac{\delta F_{\mathrm{el}}}{\delta\phi}\right)=\Theta. \tag{6}$$

Reference 10 concluded that $S(q)$ was affected by the polymer elastic terms at $O(\dot{\gamma}^2)$, and that T_c was indeed shifted to higher temperatures by the shear flow.

More generally, the two papers may be regarded as presenting competing versions of "polymer solution hydrodynamics." Because entangled polymer solutions have long characteristic times for relaxation of elastic stresses, conventional hydrodynamics for polymers (i.e., neglect of elastic effects) is valid only for extremely low frequencies. To increase the frequency range of polymer hydrodynamics, one must include some equation for the time evolution of the elastic polymer stress, i.e., for the distortion of the polymer coils by the flow and their relaxation. If the stress relaxation time is well separated from other microscopic relaxation times (e.g., for well-entangled reptating chains, the reptation time τ_{rep} is much longer than the Rouse time τ_R for primitive path fluctuations[12]), the hydrodynamic regime of frequencies is thereby greatly extended. Dynamical equations for polymer elastic stresses have a long history; convenient differential-equation forms for viscoelastic constitutive equations have been obtained by Marrucci.[13] Once the polymer stress (or equivalently, a strain variable) has been added to the set of hydrodynamic variables, the coupling of this variable to the polymer concentration must be obtained. The physics of entangled polymer solutions in flow which is not present in the rheology of polymer melts is precisely this: that the polymer elastic stresses may induce relative flow of polymer and solvent, i.e., polymer diffusion currents. When the stress relaxation time is long and the osmotic compressibility of the polymer is large, as for entangled solutions near T_c, one may expect large elastically induced polymer concentration variations in a shear flow.

The two questions which this paper answers are (1) which of the HF (Ref. 7) and Onuki (Ref. 10) theories is the correct description of polymer hydrodynamics for Rouse chains and (2) how does the model change when extended to reptation kinetics?

To answer the first question, we derive the hydrodynamic equations for the Rouse model in a different way from HF, which turns out to expose a shortcoming of the phenomenology of Ref. 10. We present the Rouse equations, which are coupled Langevin equations for the positions of the beads on a Rouse chain, as the equivalent Fokker-Planck (FP) equation for the phase-space distribution function of the entire set of microscopic chain variables (denoted by c),

$$\frac{\partial P(c)}{\partial t} = \partial_c \cdot \Lambda(c) \cdot \left[T\partial_c + \frac{\delta F_R}{\delta c} \right] P(c) . \tag{7}$$

We then employ a procedure developed by Kawasaki and Sekimoto[14] for projecting a FP equation for the distribution function of microscopic phase-space variables to an FP equation for the distribution function of the hydrodynamic variables. We take the set of variables to be the monomer concentration $\phi(x)$, the momentum density $g_j(x)$, and a strain variable $w_{ij}(x)$ defined similarly to Ref. 10 in that $T\phi w \equiv \Pi^{(e)}$. The basic idea is to (1) integrate the FP equation over the microscopic variables while constraining the hydrodynamic variables to a particular value, and (2) make the local equilibrium approximation that the microscopic variables quickly relax to the state of equilibrium consistent with the local values of ϕ, w_{ij}, and g_j.

From the projected FP equation, one can convert back to coupled Langevin equations for ϕ, w_{ij}, and g_j, which are the desired hydrodynamic equations. Our main interest is in the Onsager coefficients, since it is here that the two models disagree. These Onsager coefficients form a matrix both in space coordinates $\{r, r'\}$ and in the variables $\{\phi, w_{ij}\}$. The expression for the projected Onsager coefficients from Ref. 14 is

$$\Lambda^{\phi w}_{rr'}\{\phi, w\} = \left\langle \frac{\partial \hat{\phi}(r)}{\partial c} \cdot \Lambda(c) \cdot \frac{\partial \hat{w}(r')}{\partial c} \right\rangle_{\{\phi, w\}} , \tag{8}$$

and similarly for $\Lambda^{\phi\phi}$. This leads to a concentration equation

$$\frac{\partial \phi}{\partial t} + \nabla \cdot v\phi + \int dr' \left[\Lambda^{\phi\phi}_{rr'} \frac{\delta F}{\delta \phi}(r', t) + \Lambda^{\phi w}_{rr'} : \frac{\delta F}{\delta w}(r', t) \right] = \Theta , \tag{9}$$

with Onsager coefficients given by

$$\begin{aligned} &\Lambda^{\phi\phi}_{rr'} = \zeta^{-1} \nabla_r \cdot \nabla_{r'} [\phi(r)\delta(r - r')] , \\ &\Lambda^{\phi w}_{rr'} = \zeta^{-1} \phi^{-1}(r') \nabla_{r'} \cdot w_{ij}(r') \nabla_r [\phi(r)\delta(r - r')] + \zeta^{-1} \nabla_i \nabla_l [w_{jl}(r)\delta(r - r')] + \zeta^{-1} \nabla_j \nabla_l [w_{il}(r)\delta(r - r')] . \end{aligned} \tag{10}$$

The existence of off-diagonal Onsager couplings is a strong indication of what is amiss with the concentration equation of Ref. 10. To see this, we combine the two dissipative terms of Eq. (9); part of the off-diagonal term cancels the elastic term of Eq. (6), leaving

$$\frac{\partial \phi}{\partial t} + \nabla \cdot v\phi + \zeta^{-1} \nabla \cdot \phi \nabla \frac{\delta F_O}{\delta \phi} + 2\zeta^{-1} \nabla\nabla : w \cdot \frac{\delta F_{\text{el}}}{\delta w} = \Theta . \tag{11}$$

We may identify the last term as precisely the elastic term of the HF concentration equation, by the following argument. Under an affine deformation $\mathbf{r}' = E \cdot \mathbf{r}$, the polymer strain variable w is mapped to $w' = E \cdot w^{(0)} \cdot E^T$, where the equilibrium value for the strain tensor is $w^{(0)}_{ij} = \delta_{ij}$. Now, the general expression for the stress in a medium under finite deformation is $\Pi = (\delta F/\delta E) \cdot E^T$, and in fact the free energy F is only a function of the Cauchy-Green strain tensor $C = E \cdot E^T$. This leads to $\Pi = (2\delta F/\delta C) \cdot C = 2w \cdot \delta F/\delta w$. (This result may also be obtained by computing the projected free energy F

$=\ln\langle\exp(-F_R)\rangle_{\{\phi,w\}}$; for the Rouse model, the result is $F=\int dV[f(\phi)+\frac{1}{2}\phi\,\mathrm{tr}(w-\ln w)]$.) Hence, for the Rouse model, the HF expression for the polymer concentration equation of motion is correct, while the Onuki expression neglects the off-diagonal Onsager coefficients.

At this point it is worth noting an apparent paradox regarding the motion of Rouse chains in shear flow, and its resolution. To consider the center-of-mass (c.m.) motion of a single Rouse chain, we sum the Rouse equation over beads, eliminating all effect of intrachain spring forces. For a constant average density we obtain

$$\frac{\partial\langle R_{\mathrm{c.m.}}\rangle}{\partial t}=\frac{1}{N}\int ds\, v(R(s))\,. \qquad (12)$$

Hence the average Rouse c.m. velocity is equal to the bead-averaged fluid velocity at any instant. If the shape of the Rouse chain stays roughly constant in time, then the chain c.m. must move with the fluid [up to terms of order $O(\nabla_i\nabla_j v)$].[15] How then can there be a monomer current as in Eq. (3) which depends explicitly on elastic forces, since the current of c.m. positions is independent of elastic forces?

The resolution of this paradox depends on contributions to the monomer current which come from variations in space of the local average shape of chains. Suppose we have a constant density of c.m. positions $\phi_{\mathrm{c.m.}}(x)=\phi_0$, while the monomers of a chain with c.m. at x_0 are distributed about x_0 in a normalized cloud $C(x-x_0;x_0)$. The shape of the monomer cloud varies with its c.m. position, and is given by $\Sigma_{ij}(x_0)=\int dx\, C(x;x_0)x_ix_j$. Then the monomer density is given by

$$\begin{aligned}\rho(x)&=\phi_0\int dx_0\, C(x-x_0;x_0)\\&\approx\phi_0[1+\tfrac{1}{2}\nabla_i\nabla_j\Sigma_{ij}(x)]\,.\end{aligned} \qquad (13)$$

This illustrates that the monomer density may differ from the chain c.m. density precisely when the chains are distorted inhomogeneously in space, and hence the monomer and c.m. position currents may differ as well.

The interesting experiments on shear dependence of scattering in polymer fluids are typically carried out in well-entangled solutions, for which the Rouse model is inappropriate. We must therefore extend the concentration equation (11) to the case of reptation dynamics. Rather than projecting the FP equation for microscopic reptation kinetics onto hydrodynamic variables,[16] we shall pursue a more physical approach, of considering the polymer-solvent system as a generalized two-fluid model. Such models have been previously employed, e.g., to study dynamic fluctuations of semidilute polymer solutions.[17–19]

Instead of focusing on the kinetics of a single chain in the solution as for the Rouse case, we instead consider the forces acting on a small volume of semidilute solution. We incorporate the following stresses into the equations: (1) Monomer-monomer interactions, which we take to be a function of concentration *only*: $\Pi^{(o)}=-\mu(\phi)\delta_{ij}$. Having ruled out the mechanism of Ref. 10 for the Rouse model, we assert that the chemical potential does not depend on local strain for entangled chains, if swelling effects are small.[20] (2) Chain elastic stresses, which have a microscopic stress tensor $\Pi^{(e)}$ in the general case given by Eq. (4). These forces are communicated down chain backbones. (3) Fluid stresses $\Pi^{(f)}$, including solvent shear stress $\frac{1}{2}\eta_s(\nabla_i v_j+\nabla_j v_i)$ and hydrostatic pressure $-p\delta_{ij}$ (which enforces incompressibility of the solvent plus polymer). In well-entangled solutions, only the fluid pressure is significant. (4) Large drag forces between fluid and polymer when relative motion is present. For the Rouse model this is just Stokes drag on each bead; in general, we may think of a Darcy coefficient $\Gamma^{-1}(\phi)$ in the two-fluid model.

We may write equations of motion for the polymer and fluid mass and momentum densities, and the polymer strain variable, as (here $\rho_p=m\phi$, m is the monomer mass)

$$\begin{aligned}&\dot\phi+m^{-1}\nabla\cdot g_p=0,\quad \dot\rho_f+\nabla\cdot g_f=0\,,\\&\dot g_p-\nabla\cdot\Pi^{(o)}-\nabla\cdot\Pi^{(e)}-\Gamma(\phi)(v_f-v_p)=0\,,\\&\dot g_f-\nabla\cdot\Pi^{(f)}+\Gamma(\phi)(v_f-v_p)=0\,.\end{aligned} \qquad (14)$$

The polymer and fluid momentum densities are not separately conserved; they are coupled by the large drag term which causes the two velocities to remain nearly equal.

The reason for writing the equations this way, as opposed to writing one equation for the conserved total momentum density $g=g_f+g_p$ (in which the polymer-fluid drag forces cancel), is that we have physical insight as to the form of the forces acting on the fluid and polymer separately. The polymer osmotic and elastic forces act directly on g_p, while the solvent viscosity and pressure terms act on g_f.

Having written these equations, we promptly seek to eliminate explicit reference to g_p and v_p in favor of equivalent diffusion fluxes in the conservation equation for ρ_p. Because $\rho_p\ll\rho_f$ in semidilute solution, we drop the inertial term in the polymer momentum equation, and solve for $m^{-1}g_p=\phi v_p$ as

$$m^{-1}g_p\approx\phi v_f+\zeta^{-1}(\phi)(\nabla\cdot\Pi^{(o)}+\nabla\cdot\Pi^{(e)})\,, \qquad (15)$$

where we have defined $\zeta(\phi)\equiv\phi^{-1}\Gamma(\phi)$.

We may then substitute for g_p in the ϕ equation, retain only the total momentum-conservation equation, and enforce incompressibility of the total system; the result is[21]

$$\begin{aligned}&\dot\phi+\nabla\cdot v\phi-\nabla\cdot\zeta^{-1}\phi\nabla\frac{\delta F}{\delta\phi}+\nabla\cdot\zeta^{-1}\nabla\cdot\Pi^{(e)}=0\,,\\&\dot g-\nabla\cdot\Pi^{(f)}+\zeta^{-1}\phi\nabla\frac{\delta F}{\delta\phi}-\nabla\cdot\Pi^{(e)}=0,\quad\nabla\cdot g=0\,.\end{aligned} \qquad (16)$$

The osmotic and elastic force densities $\nabla\cdot\Pi^{(o)}=-\nabla\mu$ and $\nabla\cdot\Pi^{(e)}$ acting on the polymer induced relative flow between polymer and solvent. We call the flow induced by osmotic pressure a (cooperative) diffusion current when it appears in Eq. (16), while in Eq. (15) it results in a nonzero relative velocity between polymer and solvent. The novel effect in the present case of a viscoelastic solution is that the elastic force density $\nabla\cdot\Pi^{(e)}$ may also produce a monomer current. The divergence of this current is the source term proportional to $\nabla\nabla:\Pi^{(e)}$ in the concentration equation.

For the Rouse model, it is evident that the drag coefficient Γ is given by $\Gamma=6\pi\eta a\phi$, which leads directly to the HF result, with $\zeta=6\pi\eta a$. However, we are no longer limited to considering the Rouse model. In particular, we are free to take $\Gamma\sim\eta/\xi_H^2(\phi)$, which is not in general proportional to ϕ. (In Θ solvents, e.g., $\Gamma\sim\eta\phi^2$; in good solvents, $\Gamma\sim\phi^{2\nu/(3\nu-1)}$.[22]) This leads to the more general source terms in the concentration equation (16).

To complete the model for reptating chains, we may then choose an equation of motion for the polymer strain appropriate to reptation, which shows shear-dependent viscosities and normal stresses.[13]

We have given a derivation for the Rouse model of the matrix of Onsager coefficients which occur in the coupled Langevin equations of polymer solution hydrodynamics; this derivation makes clear the importance of the off-diagonal Onsager couplings, which were not included in Ref. 10. We have also presented general, physical arguments in terms of a two-fluid model as to the form of polymer hydrodynamics for entangled chains, and find that the coupling of polymer elastic stresses to the polymer concentration is of essentially the same form.

For the experiments in progress on entangled chains in shear flow, we may conclude that the results of HF at fixed q and sufficiently low shear rates ($\dot\gamma\tau_{\rm rep}\ll 1$) apply qualitatively to semidilute polymer solutions; in particular, the steady-state $S(q)$ at low shear rates will be altered according to[23]

$$[S(q,\dot\gamma)-S(q)]/S(q)\approx 2T^{-1}k_xk_y\dot\gamma\,\partial\eta/\partial\phi\,.$$

The values of the coefficients appropriate to the entangled case are of course quite different from the Rouse case; because we may have $\tau_{\rm rep}\gg\tau_R$, and hydrodynamic screening implies $1/\xi_H^2\ll a\phi$, we may expect a semidilute system to be much more sensitive to shear than a Rouse model at the same concentration and molecular weight. (The stress relaxation time is greatly increased, so that elastic stresses build up, while the fluid drag coefficient is greatly reduced by screening, so that relative motion of polymer and solvent is enhanced.)

The important question of what predictions this model makes for experiments on polymer solutions under shear for higher shear rates ($\dot\gamma\tau_{\rm rep}\gg 1$), and the limits of applicability of the model in the high shear regime, are subjects for future work.

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Note added.—A similar two-fluid model has been proposed by Doi for problems of polymer migration and phase separation in semidilute solutions under shear.[24] Onuki in a subsequent publication[25] has adopted a model similar to the two-fluid model presented here and in Ref. 24.

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