Modeling of the Rheology and Flow-Induced Concentration Changes in Polymer Solutions

Vlasis G. Mavrantzas and Antony N. Beris
Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

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The hydrodynamics of polymer solutions is modeled using a newly developed, thermodynamically consistent, generalized bracket formulation. This continuum thermodynamic development clarifies the connection between the physical assumptions introduced in previous models (by Helfand and Fredrickson, Onuki, Doi, and Milner) and the final governing equations. A quantitative description of the coupling between elastic stresses and concentration changes as well as the modeling of interphases is provided. The resulting equations describe the same phenomenology as the previous works; however, they are quantitatively different.

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The phase-separation behavior of dilute and semidilute polymer solutions under shear flow has attracted considerable attention in the literature [1-3]. The proposed theories attempted to couple the internal deformation state and the number density of the polymeric molecules in the description of the rheology and mass transfer. Moreover, independently, Doi [4] and, more recently, Bhave, Armstrong, and Brown [5] arrived at a similar set of equations in an effort to describe stress-induced concentration [4,5] and conformation [5] changes in flows of dilute polymer solutions. In all of these works, there are certain ambiguities in the derivation of the equations. In addition, there are several quantitative differences among the proposed models.

The present contribution offers an alternative approach based on a generalization of the Poisson bracket theory to account for dissipative mechanisms [6-8]. The Lie-Poisson bracket theory for continua is based on Arnold's original idea of representing the Euler equations for ideal fluid flow in a Hamiltonian form [9]. Since then, it has been applied with great success to determine the Hamiltonian structures of many of the conservative systems of differential equations arising in fluid mechanics, plasma physics, etc. [10,11]. Its main usage in conservative systems has been in the implementation of stability analyses [12]. More recently, the Hamiltonian description of dissipative systems has been made possible through the use of a generalized bracket involving the Poisson bracket together with a dissipation bracket [6-8,13,14]. The main utility of the generalized bracket for dissipative problems is in the development of constitutive models for material behavior [8], as it is used here.

We start first with a general, continuum fluid model in which the independent variables are the densities of the solution and the polymer, ρ and ρ_1, respectively, the velocity $\mathbf{u}$, and an internal structural parameter $\underline{C}=\rho_1\underline{c}$, characteristic of the polymer molecules conformations. For a Rouse chain, $\underline{c}$ can be identified with the second moment of the end-to-end distance vector of the polymers. The corresponding Hamiltonian involves the kinetic-energy density defined as $h_k=M^2/\rho$, where $\mathbf{M}$ is the momentum density, $\mathbf{M}=\rho\mathbf{u}$, and a general internal free-energy density, $h_e(\rho_1,\underline{C},\nabla\rho_1)$. In the most general case considered here, h_e is assumed to involve three types of contributions. First, a Flory-Huggins term accounting for entropic and enthalpic contributions due to mixing of the polymer with the solvent, second, an intramolecular free-energy term accounting for the departure of the polymer conformation from the equilibrium one, and third, a term depending on the polymer concentration gradient accounting for "free-surface" type of interactions. A typical expression for h_e is

$$H=\int \tfrac{1}{2}\rho u^2 dV+\int k_B T(n\ln\phi+n_s\ln\phi_s)dV$$
$$+\int \tfrac{1}{2}K\,\mathrm{tr}(\underline{C})dV-\int \tfrac{1}{2}nk_BT\ln\det\left(\frac{\underline{C}}{nk_BT/K}\right)dV$$
$$+\int \tfrac{1}{2}K_1(\nabla\phi)^2 dV. \tag{1}$$

In Eq. (1), ϕ is the volume fraction of the polymer, ϕ_s the volume fraction of the solvent, n the polymer number density, and n_s the solvent number density.

The Poisson bracket generates the convective terms in the final equations while the dissipation bracket is responsible for additional terms that specify the couplings of the various transport mechanisms. To a first-order approximation (near equilibrium) and ignoring entropy correction terms, the dissipation bracket can be taken to be a bilinear expression in F and G:

$$[F,G]=-\int \frac{\eta}{2}\left(\nabla_\alpha\frac{\delta F}{\delta M_\beta}+\nabla_\beta\frac{\delta F}{\delta M_\alpha}\right)\left(\nabla_\alpha\frac{\delta G}{\delta M_\beta}+\nabla_\beta\frac{\delta G}{\delta M_\alpha}\right)dV-\int \Lambda_{\alpha\beta\gamma\epsilon}\frac{\delta F}{\delta C_{\alpha\beta}}\frac{\delta G}{\delta C_{\gamma\epsilon}}dV-\int D_{\alpha\beta}\nabla_\alpha\frac{\delta F}{\delta\rho_1}\nabla_\beta\frac{\delta G}{\delta\rho_1}dV$$
$$-\int E_{\alpha\beta\gamma\epsilon}\left[\nabla_\alpha\left(C_{\beta\lambda}\frac{\delta F}{\delta C_{\lambda\gamma}}\right)\nabla_\epsilon\frac{\delta G}{\delta\rho_1}+\nabla_\alpha\left(C_{\beta\lambda}\frac{\delta G}{\delta C_{\lambda\gamma}}\right)\nabla_\epsilon\frac{\delta F}{\delta\rho_1}\right]dV-\int B_{\alpha\beta\gamma\epsilon\zeta\eta}\nabla_\alpha\left(C_{\beta\lambda}\frac{\delta F}{\delta C_{\lambda\gamma}}\right)\nabla_\epsilon\left(C_{\zeta\mu}\frac{\delta G}{\delta C_{\mu\eta}}\right)dV. \tag{2}$$

Here, η, $\underline{\Lambda}$, $\underline{D}$, $\underline{E}$, and $\underline{B}$ are phenomenological coefficients describing the solution viscosity, relaxation phenomena, diffusion due to concentration gradients, diffusion due to stress gradients, and dissipation driven by large gradients in the conformation of polymers, respectively. Note that the various couplings implied in Eq. (2) which emerge naturally within the generalized bracket formalism are consistent with the principle of thermodynamic equipresence [15].

Based on the above expression and the Poisson bracket [8], the resulting evolution equations for an incompressible flow are

$$\frac{\partial \rho_1}{\partial t} = -u_\beta \nabla_\beta \rho_1 + \nabla_\alpha \left(D_{\alpha\beta} \nabla_\beta \frac{\delta H}{\delta \rho_1} \right) + \nabla_\epsilon \left(\tfrac{1}{2} E_{\alpha\beta\gamma\epsilon} \nabla_\alpha \sigma_{\beta\gamma} \right) , \tag{3}$$

$$\frac{\partial M_\alpha}{\partial t} = -u_\beta \nabla_\beta M_\alpha - \nabla_\alpha p - \nabla_\beta \left(\frac{\partial h_e}{\partial(\nabla_\beta \rho_1)} \nabla_\alpha \rho_1 \right) + \nabla_\beta \sigma_{\alpha\beta} + \nabla_\beta [\eta(\nabla_\beta u_\alpha + \nabla_\alpha u_\beta)] , \tag{4}$$

$$C_{\alpha\beta_{(1)}} = -\Lambda_{\alpha\beta\gamma\epsilon} \frac{\delta H}{\delta C_{\epsilon\gamma}} + C_{\alpha\gamma} \nabla_\epsilon \left(E_{\epsilon\gamma\beta\lambda} \nabla_\lambda \frac{\delta H}{\delta \rho_1} \right) - C_{\alpha\gamma} \nabla_\epsilon \left[B_{\epsilon\gamma\beta\lambda\zeta\eta} \nabla_\lambda \left(C_{\zeta\mu} \frac{\delta H}{\delta C_{\mu\eta}} \right) \right] , \tag{5}$$

where the subscript (1) denotes the upper-convected time derivative [7], the polymeric contribution to the stress is defined as

$$\sigma_{\alpha\beta} = 2 C_{\alpha\gamma} \frac{\delta H}{\delta C_{\gamma\beta}} , \tag{6}$$

and the Einstein summation convention has been assumed over repeated Greek indices.

The momentum equation, Eq. (4), is quite standard, except for the presence of an additional term, in the form of a stress, that arises from the dependence of the Hamiltonian on $\nabla\rho_1$. The evolution equation for the conformation tensor $\underline{\mathbf{C}}$ is also a standard one [7] with the exception of the second term on the right-hand side (rhs) which couples $\underline{\mathbf{C}}$ with the chemical potential. This term is absent in previous works [2,5]. Intrachain hydrodynamic effects can very naturally be modeled through the selection of an appropriate relaxation tensor $\underline{\mathbf{\Lambda}}$. Indeed, as it is explained in Ref. [7], the following choice for $\underline{\mathbf{\Lambda}}$ provides an accounting of hydrodynamic interactions between the beads of a Hookean dumbbell model which corresponds (in the lowest order of approximation) to the one-relaxation mode abstraction of the Rouse chain used here,

$$\Lambda_{\alpha\beta\gamma\epsilon} = \frac{2}{n\zeta} [c_{\alpha\gamma}(\delta_{\beta\epsilon} - \zeta\Omega_{\beta\epsilon}) + c_{\alpha\epsilon}(\delta_{\beta\gamma} - \zeta\Omega_{\beta\gamma}) + c_{\beta\gamma}(\delta_{\alpha\epsilon} - \zeta\Omega_{\alpha\epsilon}) + c_{\beta\epsilon}(\delta_{\alpha\gamma} - \zeta\Omega_{\alpha\gamma})] , \tag{7}$$

where $\underline{\mathbf{\Omega}}$ is the Oseen-Burgers tensor [16], which may be reexpressed in terms of the second-moment tensor $\underline{\mathbf{c}}$ simply enough as

$$\Omega_{\beta\epsilon} = \langle \Omega^a_{\beta\epsilon} \rangle = \frac{3h}{4\zeta} \left(\frac{\pi k_B T}{K \operatorname{tr} \underline{\mathbf{c}}} \right)^{1/2} \left(\delta_{\beta\epsilon} + \frac{c_{\beta\epsilon}}{\operatorname{tr} \underline{\mathbf{c}}} \right) , \tag{8}$$

where $h \equiv (\zeta/6\eta_s)(K/\pi^3 k_B T)^{1/2}$ measures the strength of the hydrodynamic interaction and is typically believed to lie within the range $0.0 \le h \le 0.3$. When $h = 0.0$, the Oseen-Burgers tensor vanishes and the model reduces back to the simple Hookean dumbbell case. This represents closely the "consistently averaged" hydrodynamic effect considered by Öttinger and others [16–18]. As seen in Ref. [7], the resulting model, although not perfect, provides a very good first approximation of the main hydrodynamic effects in the polymer rheology. Namely, it results in the prediction of a shear thinning viscosity and first normal stress coefficient [18]. Higher-order approximations of viscoelasticity, including multimode models and/or a Gaussian approximation for the hydrodynamic interactions [19], may also be used, if so wished, at the expense of complicating the final equations.

However, the major outcome of the formulation is Eq. (3), the evolution equation for the polymer density. This shows that the driving forces for the mass flux of polymer molecules are, in general, both the gradient of the chemical potential, $\nabla(\delta H/\delta\rho_1)$, and the gradient of the extra stress, $\nabla \cdot \underline{\boldsymbol{\sigma}}$. To determine the exact magnitude of these contributions one has to resort to a microscopic picture for the polymer molecules. Over the past years this has led to the development of various models for describing hydrodynamics of polymer solutions. Among them, the two-fluid model [2,4] and two microscopic models for the Rouse chain (one based on the Langevin equations for the positions of the beads [3] and the other on the kinetic theory [5]) appear to be the most significant. It is very important to note here that all of these approaches lead to the same expressions for the coefficients [obtained by direct comparison of Eq. (5) with their flux equation] $\underline{\mathbf{D}}$ and $\underline{\mathbf{E}}$:

$$\begin{aligned} D_{\alpha\beta} &= (1/2\zeta)\rho_1\delta_{\alpha\beta} , \\ E_{\alpha\beta\gamma\epsilon} &= (1/\zeta)\delta_{\alpha\beta}\delta_{\gamma\epsilon} , \end{aligned} \tag{9}$$

where ζ is a viscous friction coefficient which is of the order $6\pi\eta_s\xi^{-2}$ in theta solvents, where η_s is the solvent viscosity and $\xi \sim 1/\phi$ the blob size [2].

The adoption of a two-fluid model is equivalent to the notion of two interpenetrating continua. The interactions between the two components can vary from very vigorous, leading to a complete equilibration of momentum and energy associated with the one-fluid, two-component model described above, to very weak, leading to separate momenta and thermal energies as the ones often associated with the electrons and the neutrals in a dilute plasma [20]. The case of dilute polymer solutions can be considered as an intermediate one, where complete thermal but only partial momentum equilibration is established between the macromolecules and the solvent. Two-fluid model descriptions in terms of hydrodynamic equations of motion have quite successfully been applied in the past to condensed phase systems, such as charged and neutral superfluids, and dielectric and magnetic crystals [21].

In the two-fluid model, the independent variables are the polymer density, and the conformation tensor $\underline{\mathbf{C}}=\rho_1\underline{\mathbf{c}}$, as before, but also the two momentum densities $\mathbf{M}_+$ and $\mathbf{M}_-$ corresponding to the total, ρ, and the reduced, $\rho_-\equiv\rho_1\rho_2/\rho$, densities, respectively. Then, in the dissipation bracket represented by Eq. (2), the third and fourth of the five terms are replaced by

$$-\int Z_{\alpha\beta}\frac{\delta F}{\delta M_{-\alpha}}\frac{\delta G}{\delta M_{-\beta}}dV\,, \tag{10}$$

where a new tensorial parameter, the drag coefficient tensor $\underline{\mathbf{Z}}$ is introduced. $\underline{\mathbf{Z}}$ is constrained to be a symmetric and non-negative definite tensor from the Onsager symmetry relations and the principle of non-negative entropy production, respectively. This is the simplest approximation assumed for describing the interactions between the two media [20]. Whether it is adequate to capture the complex character of the polymer-solvent interactions anticipated due to the large number of the internal degrees of freedom of the macromolecules is a subject that deserves further investigation.

Under certain simplifications, such as the neglect of inertial effects in the evolution equation for the reduced momentum density, valid for viscous, incompressible flows, it can be shown [8] that Eq. (10) leads to the following diffusion equation for ρ_1:

$$\frac{\partial\rho_1}{\partial t}=-\nabla_\beta(u_\beta\rho_1)+\nabla_\epsilon\left\{Y_{\epsilon\beta}\left[\nabla_\beta\Pi-\nabla_\gamma\left(2C_{\beta\alpha}\frac{\delta H}{\delta C_{\alpha\gamma}}+\rho_1\nabla_\beta\frac{\partial h_e}{\partial(\nabla_\gamma\rho_1)}\right)\right]\right\}, \tag{11}$$

where $\phi\equiv\rho_1/\rho_0$, $\underline{\mathbf{Y}}\equiv\rho_1(1-\phi)^2\underline{\mathbf{Z}}^{-1}$ is the diffusion tensor, and Π, the osmotic pressure, is defined as

$$\Pi=\rho_1\frac{\partial h_e}{\partial\rho_1}+(\nabla_\beta\rho_1)\frac{\partial h_e}{\partial(\nabla_\beta\rho_1)}+C_{\gamma\beta}\frac{\partial h_e}{\partial C_{\gamma\beta}}-h_e\,. \tag{12}$$

The equations for the total momentum density and the evolution of the conformation tensor are similar to Eqs. (4) and (5) above.

Equations (3) and (11) show that both the single- and two-fluid models developed using the generalized bracket formalism lead to similar equations. The two-fluid equation, Eq. (11), is more limited because of the underlying assumptions for the mechanisms that govern the concentration profile in flows of polymer solutions. However, it simultaneously conveys more information: First, the diffusion coefficients $\underline{\mathbf{D}}$ and $\underline{\mathbf{E}}$ can be extracted in a form consistent with the previous two-fluid models shown in Eq. (9) [within a factor of $(1-\phi)^2$] if the drag coefficient tensor is assumed to be isotropic. A nonisotropic form dependent on the polymer conformation tensor $\underline{\mathbf{c}}$ might better represent the polymer-solvent interactions, especially far from equilibrium. Second, from the definition of the osmotic pressure Π, Eq. (12), and the fact that the elastic part of h_e is a linear function of the polymer density ρ_1, Eq. (1), only the nonelastic part of the free-energy density h_e appears in the driving force for the two-fluid model. This is in agreement with the work of Helfand and Fredrickson [1].

In the absence of dependencies of h_e on the polymer concentration gradient $\nabla\rho_1$, our two-fluid model concentration equation is astonishingly similar to those of Helfand and Fredrickson [1], Onuki [2], Milner [3], and Doi [4]. Where our results are qualitatively different from all previous works is in the evaluation of the effects of terms that relate to surface-tension contributions in phase-separated systems. Both the single- and two-fluid models show that such interphase-related interactions manifest themselves in two ways: They act as an additional stress into the momentum equation [third term on the rhs of Eq. (4)], and they modify the equation for the osmotic pressure [second term on the rhs of Eq. (12)]. Notice that the last contribution preserves the symmetry of the other terms. These gradient contributions are different from the previously proposed ones [1,2].

The two previous microscopic approaches to the problem [3,5] are both based on the Rouse chain model and lead to equations that are similar to the ones corresponding to the two-fluid model presented here. In particular, their expressions for $\underline{\mathbf{D}}$ and $\underline{\mathbf{E}}$, Eq. (9), are the same as the ones derived from the two-fluid model above. This suggests that their modeling assumptions are very similar to that of interpenetrating continua. Indeed, all the elasticity is assumed to be confined within the chain or dumbbell. Additionally, according to Eqs. (35) and (43) in Bhave, Armstrong, and Brown [5], the transport coefficient $\underline{\mathbf{B}}$ is given as

$$B_{\alpha\beta\gamma\epsilon\zeta\eta}=(1/2\zeta)\delta_{\alpha\epsilon}\delta_{\beta\zeta}\delta_{\gamma\eta}\,. \tag{13}$$

Two more points are worth mentioning about the work of Bhave, Armstrong, and Brown [5]. First, there are some subtle differences from the bracket formalism: The constitutive equation for the structure tensor lacks a term which arises from the coupling of stresses with polymer concentration, the second term in the rhs of Eq. (5). Moreover, their mass flux equation, Eq. (35) in Bhave, Armstrong, and Brown [5], involves an additional "inertial" term, $-m/2\nabla\cdot\underline{\mathbf{c}}\cdot\nabla\mathbf{v}$, which is absent in our formulation. Second, Bhave, Armstrong, and Brown [5] have applied their model to the study of the rheology of dilute polymer solutions next to a solid wall. However, we believe that other phenomena, namely, phenomena of thermodynamic origin, are the dominant ones and primarily control the behavior of a dilute polymer solution next to a solid wall. As shown in Mavrantzas and Beris [22], it is the free-energy increase near the wall due to loss of conformational entropy caused by the presence of the solid barrier that gives rise to phenomena such as the apparent slip in the shear flow of polymer solutions and the depletion of the interfacial region in polymer molecules. This belief is reinforced from the very good agreement of the predictions with experimental data shown for the slip velocity and the depletion phenomena as a function of the imposed shear stress and the geometrical parameters [22]. Note also that the concentration profiles shown in Bhave, Armstrong, and Brown [5] change continuously with the shear rate (or Pe in their work). In contrast, the profiles shown in Mavrantzas and Beris [22] from the entropy modification theory show a saturation at high shear rates, in agreement with both experimental observations [23] and Brownian dynamics simulations [24].

In conclusion, we find that there are more similarities than differences among the various governing equations proposed for the hydrodynamics of polymer solutions. However, we believe that further quantitative comparison of the predicted effects with experimental data, especially for the stress-induced concentration changes, is necessary in order to validate the incorporated assumptions and, in particular, that of the appropriate interaction between the components of the two-fluid mixture. We hope that the systematic methodology employed in this work can be very helpful in such an effort by providing a specific, thermodynamically consistent set of governing equations.

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