Dynamics and rheology of inhomogeneous polymeric fluids: A complex Langevin approach

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Dynamics and rheology of inhomogeneous polymeric fluids: A complex Langevin approach

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A complex Langevin framework is described for carrying out numerical simulations of coupled field equations for flow and structure of inhomogeneous polymeric fluids. The formalism permits an exact embedding of the relevant thermodynamic forces into the dynamical equations, regardless of the characteristic length scale of the inhomogeneities in the fluid. As such, it is capable of treating a wide variety of systems, such as dilute and semidilute polymer solutions, microemulsions, block copolymers, and micellar solutions, including those whose equilibrium properties and self-assembly characteristics are not well described by mean-field theory. The formalism also integrates with existing molecular and continuum descriptions of coupled stress and species concentration dynamics. In this report, we present the method for the simplest case of a homopolymer solution. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1505025]

I. INTRODUCTION

The dynamics and rheology of homogeneous polymer solutions and melts have reached mature status in which continuum and molecular theories provide a comprehensive framework with which to interpret and predict the results of measurements on fluids of practical importance.[1] In contrast, the flow characteristics of *inhomogeneous* polymeric fluids, including phase-separated polymer solutions, blends, block, and graft copolymer mesophases, emulsions, foams, and other structured complex fluid formulations are much more poorly understood and no comprehensive theoretical framework exists. Among the difficulties encountered in developing a formalism capable of quantitative description of the coupled dynamics of flow and microstructure in such systems are (1) rich free energy landscapes, allowing for arbitrary combinations of homogeneous phases, ordered and disordered mesophases, and liquid crystalline phases; (2) inhomogeneities on scales ranging from tens of ångstroms to macroscopic lengths; (3) broad distributions of relaxation times; and (4) a lack of fundamental understanding of entanglement effects in inhomogeneous systems.

In the present paper, we develop a theoretical framework that addresses difficulties (1) and (2) and that integrates with existing strategies for handling entanglement effects, multiple time scales, and conventional rheological analysis. Specifically, we build on the observation that interactions between molecules in equilibrium theories of polymeric fluids can be exactly decoupled by the introduction of suitable stochastic "chemical potential" fields.[2,3] Such field-theoretic descriptions, when solved in the saddle point approximation, have been successfully used to construct intricate "mean-field" equilibrium theories of inhomogeneous polymer phases.[4] Very recently, numerical sampling methods have been devised that provide access to the complete equilibrium

thermodynamic properties of field-theory models, in the absence of the mean-field approximation or any other simplifying assumptions.[3,5] Here we show that such sampling methods can be embedded within conventional molecular and continuum frameworks for describing the coupled concentration and stress dynamics of inhomogeneous polymers. This extension permits the equilibrium self-assembly characteristics and thermodynamic properties to be captured exactly within models of dynamics and rheology for arbitrarily complicated mixtures of polymeric and nonpolymeric components.

It has been appreciated for some time that a useful continuum description of the kinetics and rheology of inhomogeneous polymeric fluids involves coupled equations for the species number (or mass) densities, the species momentum densities, the energy density, and the elastic stress fields of the various polymeric components. Mass, momentum, and energy densities, being conserved fields, have long-wavelength components that should be included among the slowest relaxing variables in a fluid.[6] In polymeric fluids, the elastic stresses, while not conserved fields, are often slow to relax, so should also be included in the set of slow variables required to describe the dynamical response at frequencies below some desired threshold.[7–9] Finally, polymeric systems in the vicinity of phase transitions can also exhibit "critical slowing down" of one or more order parameters, e.g., liquid crystalline order parameters, which should accordingly be included in the slowly relaxing set.

Once the complete set of slowly relaxing variables has been arrived at, one is faced with the challenge of postulating a set of coupled dynamical equations that can be used to faithfully describe the interplay between flow, microstructure, and elastic stresses that occur within the fluid. The framework of irreversible thermodynamics, combined with the relevant conservation laws and symmetries of the system under consideration, places some restrictions on the form of

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these equations, but generally one is left with a cumbersome equation set involving a large number of phenomenological kinetic coefficients.[10,11] Thus, in recent years researchers have turned to molecular-based models to provide insights into the dynamical couplings that arise in inhomogeneous fluids between macrovariables. Specifically, the dissipative couplings between polymer elastic stress and polymer concentration (i.e., number or mass density) were only clearly elucidated over the past decade as a number of theoretical and experimental researchers focused attention on stress-induced diffusion effects in inhomogeneous polymer solutions and melts.[7–9,12,13]

Formal projection operator methods exist for deducing dynamical equations for macro-variables, given a molecular description of polymer dynamics.[14,15] However, as in simple fluids, the resulting equations contain memory functions that are extremely difficult to evaluate. Some progress was made by Kawasaki and Sekimoto,[16] who identified a local equilibrium approximation that directly yields memory functions (dissipative couplings) in the Markov approximation, i.e., time-independent kinetic (Onsager) coefficients. However, these expressions also prove very difficult to evaluate and the formalism has only found limited application.[17] More recently, Doi, Onuki, Milner, and co-workers have identified a "two-fluid model" approach that very efficiently generates Onsager couplings between stress and concentration variables and appears to give exact results for the *Rouse model* in the low frequency limit (Markov approximation).[9,12] For entangled inhomogeneous melts and solutions, the two-fluid approach captures the proper long-wavelength limit of the relevant Onsager couplings for the reptation model.[12,18]

In the present paper, we adopt the two-fluid model for the purpose of developing approximate coupled dynamical equations between density and stress variables, but show how exact thermodynamic driving forces for any starting microscopic model of an inhomogeneous polymeric fluid can be embedded within these equations. For this purpose, we show that it is convenient to introduce stochastic conjugate chemical potential and elastic strain fields in addition to the density and elastic stress fields that are conventionally retained. Milner[9] and Onuki[8] have previously used strain (a "conformation tensor") in place of stress in treating the dynamics of inhomogeneous polymer solutions, but their description was restricted to slow spatial variations of the strain and density fields. Maurits and Fraaije[19] have similarly used a chemical potential in place of density, but the strain and stress variables were not included in their "external potential dynamics" scheme. Our formalism generalizes and extends these approaches in a number of ways: inclusion of thermodynamic forces valid for inhomogeneities on arbitrary scales, embedding of exact equilibrium model properties, straightforward application to polymer mixtures of arbitrary complexity, and seamless connection with conventional continuum descriptions of viscoelastic phenomena.

In the present paper we elaborate the method for the simple case of a homopolymer solution. Subsequent reports will generalize the formalism to multiphase polymer blends, block copolymers, and other heterogeneous polymer solu-

tions and alloys, as well as provide the results of numerical studies on such systems.

II. EQUILIBRIUM MODELS AND PROPERTIES

For the purpose of illustrating our method, we work with a standard model of flexible polymer solutions discussed in the classic text of Doi and Edwards.[1] In particular, we adopt the "Gaussian thread model" in which polymer conformations are described by continuous space curves, $\mathbf{R}_\alpha(s)$, where $\alpha = 1,...,n$ indexes the polymer chains and s is an arc length variable running from 0 to N, the polymerization index, along each chain contour. We further work in the nVT canonical ensemble, treating the solvent as a continuum that enters thermodynamically only through the potential of mean force between polymer segments.

Conformations of noninteracting polymers are given a Gaussian statistical weight, $\exp(-U_0)$, with a "stretching" (free) energy given by

$$U_0[\mathbf{R}] = \frac{3k_BT}{2b^2} \sum_{\alpha=1}^{n} \int_0^N ds \left| \frac{d\mathbf{R}_\alpha(s)}{ds} \right|^2, \tag{1}$$

where b is the statistical segment length. Nonbonded interactions of mean force between monomers (statistical segments) on the same polymer and between monomers on different polymers are typically represented by δ-function pseudopotentials. The effective potential energy function can be written

$$\beta U_1[\mathbf{R}] = \frac{u_0}{2!} \int d\mathbf{r}[\hat{\rho}(\mathbf{r})]^2 + \frac{w_0}{3!} \int d\mathbf{r}[\hat{\rho}(\mathbf{r})]^3, \tag{2}$$

where $\beta = 1/(k_BT)$, $\hat{\rho}(\mathbf{r}) \equiv \Sigma_{\alpha=1}^n \int_0^N ds\, \delta(\mathbf{r} - \mathbf{R}_\alpha(s))$ is the microscopic monomer number density, u_0 is the excluded volume parameter, and w_0 is a parameter representing the strength of the effective three-body potential of mean force. For good solvents, $u_0, w_0 > 0$, and the three-body term is often neglected. In the case of poor solvents, however, $u_0 < 0$, $w_0 > 0$ and the three-body contribution to U_1 must be retained in order to stabilize dense polymer phases produced by phase separation. We note that self-interactions of monomers should in principle be excluded from the two-body and three-body contributions above, but they prove to have no consequence in the present Gaussian thread model. To simplify the notation, we express all energies in units of k_BT; hence, $\beta = 1$ in the remainder of the paper.

The configurational partition function of the above "standard" model of polymer solutions is expressed as

$$Z = \int \mathcal{D}[\mathbf{R}]\exp(-U_0[\mathbf{R}] - U_1[\mathbf{R}]). \tag{3}$$

The notation $\int \mathcal{D}[\mathbf{R}]$ denotes n path integrals over all possible space curves describing the conformations of the n polymer chains confined to a volume V. This model has been studied by a variety of approximate analytical techniques, including the use of mean-field approximations, perturbation expansions, and renormalization group theory.[1,20] Here we avoid such approximate methods, but instead transform the partition function by some well-known exact formal manipulations.[21,22] Since our focus in the present paper is on

the collective dynamics of density and elastic stress fields, it proves convenient to insert the following identity in the integrand of Eq. (3)

$$\int \mathcal{D}[\rho] \int \mathcal{D}[\sigma] \delta(\rho - \hat{\rho}) \delta(\sigma - \hat{\sigma}) = 1. \tag{4}$$

The integrals appearing in this equation are functional integrals over the real fields $\rho(\mathbf{r})$ and $\sigma_{jk}(\mathbf{r})$, where the subscripts $j(k) = 1, 2, 3$ indicate Cartesian indices. The functional δ functions on the right hand side (RHS) of Eq. (4) constrain the monomer density field $\rho(\mathbf{r})$ to the microscopic monomer density $\hat{\rho}(\mathbf{r})$ and the elastic polymer stress field $\sigma_{jk}(\mathbf{r})$ to the microscopic elastic stress $\hat{\sigma}_{jk}(\mathbf{r})$ at all points $\mathbf{r}$ in the volume V. The microscopic expression for the elastic stress contributed by the polymers is well known:[1]

$$\hat{\sigma}_{jk}(\mathbf{r}) = \frac{3}{b^2} \sum_{\alpha=1}^{n} \int_0^N ds \ \frac{dR_{\alpha j}(s)}{ds} \frac{dR_{\alpha k}(s)}{ds} \delta(\mathbf{r} - \mathbf{R}_\alpha(s)). \tag{5}$$

As a next step, we provide an exponential representation of the functional δ functions by introducing functional integrals over conjugate *chemical potential* $\mu(\mathbf{r})$, and *elastic strain* $\epsilon_{jk}(\mathbf{r})$, fields

$$\delta(\rho - \hat{\rho}) \delta(\sigma - \hat{\sigma})$$
$$= \int \mathcal{D}[\mu] \int \mathcal{D}[\epsilon]$$
$$\times \exp\left\{ i \int d\mathbf{r}[\mu(\rho - \hat{\rho}) + \epsilon:(\sigma - \hat{\sigma})] \right\} \tag{6}$$

where $i \equiv \sqrt{-1}$. These two steps have the effect of decoupling the conformational degrees of freedom of different chains so that the partition function can be expressed as a classical statistical field theory in the four fields ρ, μ, σ, and ϵ:

$$Z = \int \mathcal{D}[\rho] \int \mathcal{D}[\sigma] \int \mathcal{D}[\mu] \int \mathcal{D}[\epsilon]$$
$$\times \exp(-H[\rho, \sigma, \mu, \epsilon]). \tag{7}$$

The effective Hamiltonian appearing in this equation is given by

$$\beta H[\rho, \sigma, \mu, \epsilon] = \int d\mathbf{r} \ [(u_0/2!)\rho^2 + (w_0/3!)\rho^3$$
$$- i\mu\rho - i\epsilon:\sigma] - n\ln Q[i\mu, i\epsilon], \tag{8}$$

where $Q[i\mu, i\epsilon]$ denotes the partition function of a *single polymer* in the purely imaginary chemical potential and strain fields, $i\mu(\mathbf{r})$ and $i\epsilon(\mathbf{r})$. Q is formally defined as the following path integral:

$$Q[i\mu, i\epsilon] = \frac{\int \mathcal{D}[\mathbf{R}] \ \exp\left(-i \int_0^N ds \, \mu(\mathbf{R}(s)) - (3/2b^2) \int_0^N ds \, \frac{dR_j}{ds} \frac{dR_k}{ds} \{\delta_{jk} + 2i\epsilon_{jk}[\mathbf{R}(s)]\} \right)}{\left(\int \mathcal{D}[\mathbf{R}] \exp[-U_0] \right)}, \tag{9}$$

where summation over repeated Cartesian indices is implied. Equation (9) is normalized such that $Q[0,0] = 1$; this convenient choice leads to a constant shift in the Hamiltonian that is irrelevant to ensemble averages computed with the model. We are not aware of prior reports or studies of the field theory defined by Eq. (7), but closely related theories without the stress and strain fields are well known.[1,2] As a final note, the decoupling of chains affected by Eq. (6) carries through in cases other than the present nVT ensemble, so similar formulations in other ensembles are easily derived.

Analytical calculations with the field theory defined by Eq. (7) would normally proceed by some approximate evaluation of the path integral defining Q. This might involve a "Gaussian approximation," in which Q is expanded to quadratic order in the fields μ and ϵ, or a "long-wavelength approximation" in which Q is expanded in gradients of these conjugate fields.[23] Here we avoid such approximations and show in Appendix A that a Feynman–Kac formula[24,25] can

be derived for Q. Specifically, Q can be expressed as

$$Q[i\mu, i\epsilon] = \frac{1}{V} \int d\mathbf{r} \ q(\mathbf{r}, N; [i\mu, i\epsilon]), \tag{10}$$

where $q(\mathbf{r}, s; [i\mu, i\epsilon])$ is a propagator associated with the statistical weight that a piece of chain with contour length s, and experiencing the fields $\mu(\mathbf{r})$ and $\epsilon(\mathbf{r})$, terminates at position $\mathbf{r}$. (We subsequently omit the functional dependence of q on μ and ϵ to simplify the notation.) In Appendix A, we show that $q(\mathbf{r}, s)$ satisfies the following complex diffusion equation:

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = -\frac{1}{2} \text{tr} \ln[\mathbf{1} + 2i\epsilon(\mathbf{r})] q(\mathbf{r}, s) - i\mu(\mathbf{r}) q(\mathbf{r}, s)$$
$$+ \frac{b^2}{6} \nabla\nabla : [\mathbf{m}(\mathbf{r}; [i\epsilon]) q(\mathbf{r}, s)] \tag{11}$$

subject to the "initial condition" $q(\mathbf{r}, 0) = 1$, and where the tensor $\mathbf{m}$ is defined by

J. Chem. Phys., Vol. 117, No. 14, 8 October 2002

Dynamics and rheology of inhomogeneous polymeric fluids 6813

$$\mathbf{m}(\mathbf{r};[i\epsilon]) \equiv [\mathbf{1}+2i\epsilon(\mathbf{r})]^{-1}\{\det[\mathbf{1}+2i\epsilon(\mathbf{r})]\}^{-1/2}$$

$$\approx \mathbf{1}[1-i\ \mathrm{tr}\ \epsilon(\mathbf{r})]-2i\epsilon(\mathbf{r}). \tag{12}$$

In Eq. (11), $\mathbf{1}$ denotes the unit tensor and tr denotes the trace of a tensor. We have assumed that the relevant elastic strains are small in deriving the final expression in Eq. (12) since this is required for applicability of the Gaussian chain model. The corresponding diffusion equation without the strain variable ($\epsilon=0$) is well known;[24] however, to our knowledge, Eq. (11) has not been previously reported.

To summarize our results so far, a microscopic model of a polymer solution, expressed in terms of the chain conformation variables $\mathbf{R}_\alpha(s)$, has been converted into a field theory [Eq. (7)] involving four *real* fields: monomer density (ρ), polymer elastic stress (σ), and the conjugate variables of monomer chemical potential (μ) and polymer elastic strain (ϵ). The effective Hamiltonian governing the interactions between these fields is given by Eq. (8) and is generally *complex* (i.e., has both real and imaginary parts). The "entropy" term, $\ln Q[i\mu,i\epsilon]$, appearing in the effective Hamiltonian can be computed deterministically for a given realization of the μ and ϵ fields by solving the complex diffusion Eq. (11), subject to $q(\mathbf{r},0)=1$. Equilibrium ensemble averages of some quantity $G[\rho,\sigma,\mu,\epsilon]$ are computed according to

$$\langle G \rangle = Z^{-1}\int \mathcal{D}[\rho]\int \mathcal{D}[\sigma]\int \mathcal{D}[\mu]\int \mathcal{D}[\epsilon]G[\rho,\sigma,\mu,\epsilon]$$

$$\times \exp(-H[\rho,\sigma,\mu,\epsilon]). \tag{13}$$

In practice, we shall see that such averages are computed as "time averages" in a complex Langevin simulation.

Our formalism for the dynamics and rheology of inhomogeneous polymers involves constructing appropriate stochastic equations of motion for the four fields ρ,σ,μ,ϵ that are physically realistic and that generate exact equilibrium

averages consistent with Eq. (13). For this purpose it is necessary to have expressions for the relevant thermodynamic forces, which are first functional derivatives of the effective Hamiltonian with respect to the four fields. These forces can be written

$$\frac{\delta H}{\delta \rho(\mathbf{r})}=u_0\rho(\mathbf{r})+(w_0/2)[\rho(\mathbf{r})]^2-i\mu(\mathbf{r}), \tag{14}$$

$$\frac{\delta H}{\delta \sigma(\mathbf{r})}=-i\epsilon(\mathbf{r}), \tag{15}$$

$$\frac{\delta H}{\delta \mu(\mathbf{r})}=i\{\tilde{\rho}(\mathbf{r},[i\mu,i\epsilon])-\rho(\mathbf{r})\}, \tag{16}$$

$$\frac{\delta H}{\delta \epsilon(\mathbf{r})}=i\{\tilde{\sigma}(\mathbf{r},[i\mu,i\epsilon])-\sigma(\mathbf{r})\}. \tag{17}$$

The objects $\tilde{\rho}$ and $\tilde{\sigma}$ are functionals of μ and ϵ that are defined by

$$\tilde{\rho}(\mathbf{r},[i\mu,i\epsilon])=in\frac{\delta \ln Q}{\delta \mu(\mathbf{r})},$$

$$\tilde{\sigma}_{jk}(\mathbf{r},[i\mu,i\epsilon])=in\frac{\delta \ln Q}{\delta \epsilon_{jk}(\mathbf{r})}, \tag{18}$$

and, as we shall see below, can be interpreted as *auxiliary monomer density* and *auxiliary elastic stress* operators. By invoking a well-known factorization formula of the defining path integral, Eq. (9), $\tilde{\rho}$ can be computed from solutions of the complex diffusion Eq. (11):

$$\tilde{\rho}(\mathbf{r},[i\mu,i\epsilon])=\frac{n}{VQ}\int_0^N ds\,q(\mathbf{r},s)q(\mathbf{r},N-s). \tag{19}$$

In Appendix B, we show that $\tilde{\sigma}$ can also be constructed from solutions of the diffusion Eq. (11). Specifically, to first order in ϵ, $\tilde{\sigma}$ is given by

$$\tilde{\sigma}_{jk}(\mathbf{r},[i\mu,i\epsilon])=\tilde{\rho}(\mathbf{r},[i\mu,i\epsilon])[\delta_{jk}-2i\epsilon_{jk}(\mathbf{r})]-\delta_{jk}\frac{b^2}{6}\tilde{\rho}(\mathbf{r},[i\mu,i\epsilon])\boldsymbol{\nabla}\boldsymbol{\nabla}\!:\!\mathbf{m}(\mathbf{r})-\delta_{jk}\frac{nb^2}{3VQ}[\nabla_l m_{lp}(\mathbf{r})]$$

$$\times \int_0^N ds\ q(\mathbf{r},s)\nabla_p q(\mathbf{r},N-s)+\frac{nb^2}{3VQ}m_{jl}(\mathbf{r})m_{kp}(\mathbf{r})\int_0^N ds\,q(\mathbf{r},s)\nabla_l\nabla_p q(\mathbf{r},N-s), \tag{20}$$

where $\mathbf{m}(\mathbf{r})$ is the ϵ-dependent tensor introduced in Eq. (12). Again, the restriction to small strains is consistent with our use of the Gaussian chain model.

Field configurations for which the effective Hamiltonian is *stationary*, i.e., fields ($\rho^*,\mu^*,\sigma^*,\epsilon^*$) such that

$$\frac{\delta H}{\delta \rho(\mathbf{r})}=\frac{\delta H}{\delta \mu(\mathbf{r})}=\frac{\delta H}{\delta \sigma(\mathbf{r})}=\frac{\delta H}{\delta \epsilon(\mathbf{r})}=0, \tag{21}$$

play an especially important role in the theory.[3] Although the fields were introduced as real objects and the physical path of

integration in Eq. (7) is the real axis, the stationary field configurations in general lie off the real axis and correspond to *saddle points* in the complex plane. The physically relevant stationary fields ρ^* and σ^* for the present polymer solution model prove to be real, while μ^* and ϵ^* are pure imaginary. Saddle points can be either homogeneous ($\mathbf{r}$-independent) or inhomogeneous depending on the details and parameters of the starting model. Moreover, there is a topologically distinct, defect-free saddle point that can be associated with each equilibrium phase exhibited by a system. As is well known, saddle point field configurations correspond to *mean-field solutions* of statistical field theory

models.[26] The "mean-field approximation" involves the assumption that the functional integrals in Eqs. (7) and (13) are dominated entirely by a saddle point, i.e., $Z \approx \exp(-H[\rho^*,\mu^*,\sigma^*,\epsilon^*])$ and $\langle G \rangle \approx G[\rho^*,\mu^*,\sigma^*,\epsilon^*]$. Self-consistent field theory, the canonical mean-field theory for the equilibrium properties of inhomogeneous polymer phases, is derived by invoking exactly such an approximation.[24]

The interpretation of $\widetilde{\rho}$ and $\widetilde{\sigma}$ as "auxiliary" density and stress operators should now be apparent. At a saddle point, when μ and ϵ achieve their "mean-field values" μ^* and ϵ^*, it follows from Eqs. (16) and (17) that $\rho(\mathbf{r}) = \widetilde{\rho}(\mathbf{r},[i\mu^*,i\epsilon^*])$ and $\sigma(\mathbf{r}) = \widetilde{\sigma}(\mathbf{r},[i\mu^*,i\epsilon^*])$. However, when describing systems out of equilibrium, or in treating equilibrium systems without invoking the mean-field approximation, instantaneous configurations of ρ and σ will in general differ from $\widetilde{\rho}$ and $\widetilde{\sigma}$.

Average equilibrium properties of the model can be computed by means of a field-theoretic polymer simulation (FTPS).[3,5] In such a simulation the relevant fields (here ρ,σ,μ,ϵ) are discretized within a simulation cell, e.g., using finite differences, and a sampling strategy is devised that generates a Markov chain of field configurations with a statistical weight proportional to $\exp(-H[\rho,\sigma,\mu,\epsilon])$. Ensemble averages such as Eq. (13) are then computed as time averages over the states of the Markov chain. Because the effective Hamiltonian is complex, the relevant statistical weight is not positive definite and so special sampling techniques must be applied. We found previously[5] that a complex Langevin technique, developed in the context of lattice simulations for quantum and nuclear physics,[27,28] is particularly convenient for this purpose. Specifically, one extends each of the four fields to the complex plane and generates successive states by time integration of a nonconserved Langevin dynamics with a noise source applied only to the real component. For example, in the case of the field μ, one can apply the complex Langevin dynamics:

$$\frac{\partial}{\partial t}\mu(\mathbf{r},t) = -\frac{\delta H}{\delta \mu(\mathbf{r},t)} + \theta_R(\mathbf{r},t), \tag{22}$$

where it is understood that μ is to be decomposed into real and imaginary parts according to $\mu = \mu_R + i\mu_I$, as is the thermodynamic force $\delta H/\delta\mu$ given by Eq. (16). Thus, Eq. (22) actually represents a set of two real equations of motion for μ_R and μ_I. The noise source θ_R is *purely real*, and is Gaussian and white, with moments

$$\langle \theta_R(\mathbf{r},t) \rangle = 0,$$
$$\langle \theta_R(\mathbf{r},t)\theta_R(\mathbf{r}',t') \rangle = 2\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'). \tag{23}$$

The absence of a noise source in the equation for μ_I is intrinsic to the complex Langevin method; we refer the interested reader to the literature.[27,28]

There are two final important points regarding the complex nature of this formalism. First, it should be emphasized that the above complex Langevin dynamics scheme is simply an artifice to generate Markov chains with the proper equilibrium statistics. Specifically, in the case of the fields ρ and σ, the above complex Langevin dynamics *does not* represent a physically realistic dynamical evolution. Indeed, the focus of the remainder of this paper is how to modify the complex Langevin scheme to provide more a more realistic polymer dynamics, while still retaining the exact equilibrium properties of the model. The second point is that a complex formalism is unavoidable if we are unwilling to make approximations such as the mean-field approximation. One could in principle construct a purely real statistical field theory in the two fields ρ and σ, but this would require the functional integrals over the conjugate fields μ and ϵ in Eq. (7) to be carried out exactly—a feat that cannot be accomplished. Alternatively, a purely real theory in the four fields can be achieved by simply adding to Eq. (7) its complex conjugate and by noting that Z is real. However, this field theory has a nonpositive definite statistical weight proportional to $\cos(H_I)\exp(-H_R)$, so there is no advantage to avoiding a fully complex formalism. (We refer the interested reader to Ref. 3 for a more detailed discussion of this point.)

III. TWO-FLUID DYNAMICS

The complex Langevin scheme is evidently very convenient for the purpose of computing equilibrium properties of both homogeneous and inhomogeneous polymeric fluids. An important question to ask is whether we can modify the scheme in a way that leads to realistic dynamical evolution and rheological predictions out of equilibrium, while preserving the exact equilibrium properties of a model. In this section, we show that such a modification is indeed possible.

Before introducing our specific approach, it is useful to reflect on a possible simplification of Eq. (7). If it were permissible to drop the ρ^3 three-body interaction term in H (e.g., under good solvent conditions where $u_0 > 0$), *and* if an extra "anisotropic" interaction term of the form $\sigma{:}\sigma$ (a type of nematic coupling) is included, the effective Hamiltonian would be quadratic in the fields ρ and σ. It would then be possible to explicitly integrate out these two fields exactly, leaving a field theory in the two remaining conjugate fields μ and ϵ. While such a simplification would seem to be desirable, it leads to a number of difficulties. First are the restrictions this would imply on the types of interactions that could be included in a polymer model. Besides excluding poor solvent conditions in the model discussed here, the above steps cannot be performed for any starting molecular model with "hard core" pair potentials, since such potentials lack a functional inverse. A second major drawback with eliminating the ρ and σ fields is that these are the physical fields for which connections to a molecular description are available. It is more difficult to postulate a physically realistic dynamics for the retained conjugate fields μ and ϵ. Onuki[8] and Milner[9] have shown that it is possible to overcome this hurdle for the ϵ field and have constructed sensible models of elastic strain dynamics (for systems with slowly varying inhomogeneities) that mimic conventional models of stress dynamics. The problem is more serious, however, for the μ field. Upon eliminating ρ, the auxiliary density operator $\widetilde{\rho}$ can be identified with the physical density. Thus one might hope to construct a μ dynamics by means of the chain rule

J. Chem. Phys., Vol. 117, No. 14, 8 October 2002

Dynamics and rheology of inhomogeneous polymeric fluids   6815

$$\frac{\partial}{\partial t}\mu(\mathbf{r},t)=\int d\mathbf{r}'\ \frac{\delta\mu(\mathbf{r},t)}{\delta\widetilde{\rho}(\mathbf{r}',t)}\ \frac{\partial}{\partial t}\widetilde{\rho}(\mathbf{r}',t) \tag{24}$$

and a physically motivated dynamics for the density $\widetilde{\rho}$. This strategy, however, is blocked in the canonical ensemble because the object $\delta\mu(\mathbf{r},t)/\delta\widetilde{\rho}(\mathbf{r}',t)$ is singular in the long-wavelength limit. This object is the functional inverse of $\delta\widetilde{\rho}(\mathbf{r})/\delta\mu(\mathbf{r}')$, i.e.,

$$\int d\mathbf{r}'\ \frac{\delta\mu(\mathbf{r})}{\delta\widetilde{\rho}(\mathbf{r}')}\frac{\delta\widetilde{\rho}(\mathbf{r}')}{\delta\mu(\mathbf{r}'')}=\delta(\mathbf{r}-\mathbf{r}''). \tag{25}$$

Because $\delta\widetilde{\rho}(\mathbf{r})/\delta\mu(\mathbf{r}')$ can be shown to vanish upon integration over either $\mathbf{r}$ or $\mathbf{r}'$, the inverse does not have a finite limit for slow spatial variations of the field $\mu(\mathbf{r})$. Maurits and Fraaije[19] have apparently avoided this difficulty by invoking an approximation in constructing their ''external potential dynamics'' scheme; however, this approximation is inconsistent with the exact properties of the model just described.

Evidently, the above problems disappear if we agree to retain all four fields as dynamical variables. By connecting to an underlying microscopic dynamics for chain variables, one can postulate a realistic collective dynamics for the physical, ''primary'' density and stress fields. The conjugate variables of chemical potential and strain can be slaved to these primary fields with a simple and computationally convenient dynamics that preserves the exact equilibrium properties of the model. We begin by discussing the coupled dynamics of density and elastic stress.

A. Two-fluid formalism

As described in the Introduction, the two-fluid model of Milner[9] and Doi and Onuki[12] provides a useful way to physically motivate the form of Onsager couplings between density and stress that are needed to construct a theory of dynamics. This model provides dissipative couplings in agreement with exact projections of the Rouse model onto density and stress variables[29] and can be adapted as well to mimic the long-wavelength dynamics of the reptation model.[12] We adopt this approach in the following and begin with the realization that $\hat{\rho}$ is a microscopically conserved field. Hence the corresponding macrovariable ρ should satisfy a continuity equation

$$\frac{\partial}{\partial t}\rho=-\boldsymbol{\nabla}\cdot(\mathbf{v}_p\rho), \tag{26}$$

where $\mathbf{v}_p(\mathbf{r})$ is the polymer velocity field. In contrast, the microscopic elastic stress field $\hat{\sigma}$ defined in Eq. (5) is not a conserved field, but is rotated and advected by the polymer velocity according to

$$\frac{\partial}{\partial t}\sigma=-\boldsymbol{\nabla}\cdot(\mathbf{v}_p\sigma)+(\boldsymbol{\nabla}\mathbf{v}_p)^T\cdot\sigma+\sigma\cdot(\boldsymbol{\nabla}\mathbf{v}_p), \tag{27}$$

where $(\boldsymbol{\nabla}\mathbf{v}_p)^T$ denotes the transpose of the polymer velocity gradient tensor and we have substituted the macrovariable σ for the microscopic stress. This upper-convected time deriva-

tive can be deduced from exact Poisson bracket relations between the microscopic stress and the microscopic polymer momentum density.

The relevant dissipative couplings can be obtained from the two-fluid model. We follow the Doi–Onuki approach[12] of introducing a Rayleigh functional, $\mathcal{R}=W/2+\dot{H}$, which is the sum of half of the energy dissipation rate, W, and the rate of change of the effective Hamiltonian, $\dot{H}$. The model for W assumes a local, frictional coupling associated with relative motion of polymer (velocity $\mathbf{v}_p$) and solvent (velocity $\mathbf{v}_s$) and viscous dissipation in the solvent:

$$W[\mathbf{v}_s,\mathbf{v}_p]=\int d\mathbf{r}\ [\zeta(\rho)(\mathbf{v}_p-\mathbf{v}_s)^2+\eta_s\boldsymbol{\nabla}\mathbf{v}_s\!:\!\boldsymbol{\nabla}\mathbf{v}_s], \tag{28}$$

where η_s is the solvent viscosity and $\zeta(\rho)=\zeta_0\rho$ is the friction coefficient per unit volume of solution. The latter can be expressed as the product of a monomeric friction coefficient ζ_0 and the local monomer density $\rho(\mathbf{r})$. We neglect viscous dissipation of polymer because we will subsequently restrict the analysis to dilute and semidilute polymer solutions. The rate of change of the energy functional is evaluated according to the chain rule

$$\dot{H}[\mathbf{v}_p]=\int d\mathbf{r}\left(\frac{\delta H}{\delta\rho(\mathbf{r},t)}\frac{\partial\rho(\mathbf{r},t)}{\partial t}+\frac{\delta H}{\delta\sigma(\mathbf{r},t)}\!:\!\frac{\partial\sigma(\mathbf{r},t)}{\partial t}\right), \tag{29}$$

where we have only retained the time variations of the fields ρ and σ that have microscopic Poisson-bracket couplings to the polymer velocity field. Evidently W is a quadratic form in the velocities $\mathbf{v}_p$ and $\mathbf{v}_s$, while $\dot{H}$ is linear in $\mathbf{v}_p$ once Eqs. (26) and (27) have been substituted for the time derivatives appearing on the RHS of Eq. (29).

The relevant dissipative couplings with proper Onsager symmetry are generated by minimizing $\mathcal{R}[\mathbf{v}_s,\mathbf{v}_p]$ with respect to the two velocity fields, while holding the fields ρ and σ fixed. As discussed by Doi and Onuki,[12] we can conveniently introduce the constraint of solution incompressibility by including a Lagrange multiplier term, with a pressure field p appearing as the Lagrange multiplier

$$\mathcal{R}_M[\mathbf{v}_s,\mathbf{v}_p]=\mathcal{R}[\mathbf{v}_s,\mathbf{v}_p]-\int d\mathbf{r}p(\mathbf{r},t)\boldsymbol{\nabla}$$
$$\cdot[\mathbf{v}_p\rho+\mathbf{v}_s(\rho_t-\rho)], \tag{30}$$

and where ρ_t is the constant total density of polymer plus solvent. Minimization of this ''modified'' Rayleigh functional with respect to variations in the polymer and solvent velocities leads to two force balance equations. For the polymer, we have

$$0=\zeta(\mathbf{v}_p-\mathbf{v}_s)+\rho\boldsymbol{\nabla}\frac{\delta H}{\delta\rho}-(\boldsymbol{\nabla}\sigma)\!:\!\frac{\delta H}{\delta\sigma}$$
$$-\boldsymbol{\nabla}\cdot\left(2\sigma\cdot\frac{\delta H}{\delta\sigma}\right)+\rho\boldsymbol{\nabla}p, \tag{31}$$

which reflects a balance of frictional, osmotic, elastic, and pressure forces. For the solvent, the corresponding balance is

$$0=\zeta(\mathbf{v}_s-\mathbf{v}_p)-\eta_s\nabla^2\mathbf{v}_s+(\rho_t-\rho)\boldsymbol{\nabla}p. \tag{32}$$

Although not a necessary assumption, these force balance equations assume simpler forms in the case of *dilute and semidilute* solutions for which $\rho/\rho_t \ll 1$. In this limit, polymer and solvent velocities are approximately given by

$$\mathbf{v}_s \approx \mathbf{v} \equiv [\mathbf{v}_p \rho + \mathbf{v}_s (\rho_t - \rho)]/\rho_t, \tag{33}$$

where $\mathbf{v}$ is the volume averaged velocity field, and

$$\mathbf{v}_p = \mathbf{v} + \mathbf{w} \tag{34}$$

with $\mathbf{w} \equiv \mathbf{v}_p - \mathbf{v}_s$ representing the relative velocity between polymer and solvent. Reexpressing the force balances in terms of $\mathbf{v}$ and $\mathbf{w}$ leads to the equations of motion

$$\rho_v \frac{\partial}{\partial t} \mathbf{v} = \eta_s \nabla^2 \mathbf{v} + \nabla \cdot \Pi - \nabla P, \tag{35}$$

$$\rho_w \frac{\partial}{\partial t} \mathbf{w} = -\zeta \mathbf{w} + \nabla \cdot \Pi, \tag{36}$$

where ρ_v and ρ_w are average mass densities associated with the two velocity variables and Π is a stress tensor that incorporates the sum of the osmotic and elastic stresses:

$$\nabla \cdot \Pi \equiv -\rho \nabla \frac{\delta H}{\delta \rho} + (\nabla \sigma) : \frac{\delta H}{\delta \sigma} + \nabla \cdot \left(2\sigma \cdot \frac{\delta H}{\delta \sigma} \right). \tag{37}$$

We have partially restored the inertial terms in Eqs. (35) and (36) because they are not automatically generated by the variational approach and are needed in the next section to create a consistent set of stochastic differential equations within the complex Langevin framework. The field $P \equiv \rho_t p$ is the conventional hydrodynamic pressure field and is determined by applying the incompressibility condition

$$\nabla \cdot \mathbf{v} = 0. \tag{38}$$

Equations (34)–(36) produce a rich set of dissipative terms for density and stress dynamics when combined with Eqs. (26) and (27). For example, in the typical case where the inertia of the relative velocity field $\mathbf{w}$ is negligible, Eqs. (26), (34), and (36) produce a familiar convection-diffusion equation

$$\frac{\partial}{\partial t} \rho = -\mathbf{v} \cdot \nabla \rho - \frac{1}{\zeta_0} \nabla \nabla : \Pi \tag{39}$$

in which the polymer density is convected by the volume-averaged velocity and the dissipative term $\zeta_0^{-1} \nabla \nabla : \Pi$ describes both ordinary diffusion and stress-induced diffusion[7–9,12] of polymer segments [cf. Eq. (37)]. Similar convective and dissipative terms are generated by the adiabatic substitution of $\mathbf{v}_p = \mathbf{v} + \zeta^{-1} \nabla \cdot \Pi$ into the stress equation (27). Because of the symmetry of the two-fluid dissipation functional W, all such dissipative terms have the required Onsager symmetry. One important dissipative term in the stress dynamics, however, is not automatically generated by the two-fluid formalism. Specifically, the diagonal $\sigma - \sigma$ Onsager coefficient corresponding to stress relaxation in a homogeneous polymer solution is missing. This can be phenomenologically rectified, within a Markovian single stress relaxation time approximation, by augmenting the RHS of Eq. (27) with a term $-(\rho/\tau_\sigma) \delta H/\delta \sigma$, where $\tau_\sigma(\rho_0)$

is a stress relaxation time that we phenomenologically allow to depend on the average polymer number density of the solution, $\rho_0 = nN/V$.

As a final ingredient in our model of stress and density dynamics, we must postulate equations of motion for the conjugate fields ϵ and μ. These enter linearly in the thermodynamic forces, $\delta H/\delta \rho$ and $\delta H/\delta \sigma$, that drive the relaxation of density and stress, cf. Eqs. (14), (15), and (37). The simplest strategy is to assume purely relaxational, nonconserved dynamics for both fields:

$$\frac{\partial}{\partial t} \mu = -\frac{1}{\rho_0 \tau_\mu} \frac{\delta H}{\delta \mu}, \tag{40}$$

$$\frac{\partial}{\partial t} \epsilon = -\frac{1}{\rho_0 \tau_\epsilon} \frac{\delta H}{\delta \epsilon}, \tag{41}$$

where τ_μ and τ_ϵ are characteristic relaxation times. This would seem to be an overly simplistic choice of dynamics. However, the model was constructed with the fundamental assumption that the physical fields ρ and σ are the most slowly relaxing. The conjugate fields μ and ϵ, while necessary to exactly decouple the static interactions among monomers in solution, can be associated with faster relaxing chain degrees of freedom. Thus, provided that we select

$$\tau_\mu, \tau_\epsilon \ll \tau_\sigma, \tag{42}$$

the dynamics of the *physical variables* ρ and σ should be unaffected by our particular choice of μ and ϵ dynamics.

B. Complex Langevin dynamics

In the previous section, we applied the two-fluid formalism to develop a simple model for the coupled density and stress dynamics of a polymer solution. The resulting equations of motion have been constructed so that, under equilibrium conditions, the relevant fields $(\rho, \sigma, \mu, \epsilon)$ relax to their saddle point configuration $(\rho^*, \sigma^*, \mu^*, \epsilon^*)$ satisfying Eq. (21) and the velocity fields $\mathbf{v}$ and $\mathbf{w}$ relax to zero. These *deterministic* dynamics can thus be viewed as a type of dynamic mean-field theory, similar in spirit (but not in detail) with other time-dependent self-consistent field methods reported in the literature.[19,30–32] We defer a comparison of our deterministic equations with these earlier works to Sec. III C.

In order to properly embed the *exact equilibrium properties* of our starting model into the two-fluid framework and thereby avoid the mean-field approximation, we clearly need a stochastic dynamics extension of the two-fluid equations. This is complicated by the fact that H is strictly real and hence $\exp(-H)$ is positive-definite only when the conjugate fields μ and ϵ achieve their purely imaginary saddle point values. Nevertheless, this difficulty can be circumvented by means of a complex Langevin approach. In particular, as illustrated in Eq. (22), we simply extend all the relevant fields $(\rho, \mu, \sigma, \epsilon, \mathbf{v}, \mathbf{w}, P)$ to the complex plane, interpret derivatives such as $\delta H/\delta \mu$ as complex derivatives, and augment the two-fluid equations containing dissipative coefficients with *real* noise sources.

To summarize, our complex Langevin model is defined by

$$\frac{\partial}{\partial t}\rho = -\boldsymbol{\nabla}\cdot(\mathbf{v}_p\rho), \tag{43}$$

$$\frac{\partial}{\partial t}\sigma = -\boldsymbol{\nabla}\cdot(\mathbf{v}_p\sigma) + (\boldsymbol{\nabla}\mathbf{v}_p)^T\cdot\sigma + \sigma\cdot(\boldsymbol{\nabla}\mathbf{v}_p)$$

$$-\frac{\rho}{\tau_\sigma}\frac{\delta H}{\delta\sigma} + \theta_R^\sigma, \tag{44}$$

$$\rho_v\frac{\partial}{\partial t}\mathbf{v} = [\,\eta_s\nabla^2\mathbf{v} + \boldsymbol{\nabla}\cdot\Pi - \boldsymbol{\nabla}P + \theta_R^v\,]_\perp, \tag{45}$$

$$\rho_w\frac{\partial}{\partial t}\mathbf{w} = -\zeta\mathbf{w} + \boldsymbol{\nabla}\cdot\Pi + \theta_R^w, \tag{46}$$

$$\frac{\partial}{\partial t}\mu = -\frac{1}{\rho_0\tau_\mu}\frac{\delta H}{\delta\mu} + \theta_R^\mu, \tag{47}$$

$$\frac{\partial}{\partial t}\epsilon = -\frac{1}{\rho_0\tau_\epsilon}\frac{\delta H}{\delta\epsilon} + \theta_R^\epsilon, \tag{48}$$

where all fields, except the added *real* $\boldsymbol{\theta}_R$ noise sources, are complex. The supplementary equations needed to close this equation set, Eqs. (14)–(20), (34), (37), and (38), are further interpreted as complex equations and the notation $[\,\ldots\,]_\perp$ denotes the operation of taking the transverse part of a vector field (to enforce $\boldsymbol{\nabla}\cdot\mathbf{v}=0$). The real noise sources are white with zero mean and have second moments related to transport coefficients in accordance with the fluctuation-dissipation theorem (all cross-correlations vanish):

$$\langle\theta_{R,jk}^\sigma(\mathbf{r},t)\theta_{R,lm}^\sigma(\mathbf{r}',t')\rangle = (\rho/\tau_\sigma)(\delta_{jl}\delta_{km}+\delta_{jm}\delta_{kl})$$

$$\times\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{49}$$

$$\langle\theta_{R,j}^v(\mathbf{r},t)\theta_{R,k}^v(\mathbf{r}',t')\rangle = -2\,\eta_s\rho_v\delta_{jk}\nabla^2\delta(\mathbf{r}-\mathbf{r}')$$

$$\times\delta(t-t'), \tag{50}$$

$$\langle\theta_{R,j}^w(\mathbf{r},t)\theta_{R,k}^w(\mathbf{r}',t')\rangle = 2\zeta\rho_w\delta_{jk}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{51}$$

$$\langle\theta_R^\mu(\mathbf{r},t)\theta_R^\mu(\mathbf{r}',t')\rangle = 2(\rho_0\tau_\mu)^{-1}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{52}$$

$$\langle\theta_{R,jk}^\epsilon(\mathbf{r},t)\theta_{R,lm}^\epsilon(\mathbf{r}',t')\rangle = (\rho_0\tau_\epsilon)^{-1}(\delta_{jl}\delta_{km}+\delta_{jm}\delta_{kl})$$

$$\times\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'). \tag{53}$$

The above equations define a complex Langevin dynamics that can be numerically implemented to effect field-theoretic simulations of inhomogeneous polymer solutions. For example, this could be the basis for studies of viscoelastic effects on the kinetics of phase transformations (nucleation or spinodal decomposition) or for studies of shear-induced phase separation phenomena in polymer solutions. Extensions of these equations to inhomogeneous polymer melts could be used to examine the processing behavior (e.g., the interaction between flow and microstructure) of block copolymers and polymer alloys. Similar real Langevin descriptions have been proposed for such problems, but they do not embed exact equilibrium statistical mechanics and typically involve long-wavelength approximations.[9,33,34] Thus, such approaches are restricted to situations where in-

terfaces are broad compared with the characteristic size of the polymers and to situations where mean-field theory is accurate.

The mathematical theory of complex, nonlinear Langevin equations is rather primitive[35,36] and issues remain regarding conditions for existence and uniqueness of stationary solutions. However, in our experience to date with simulations of block copolymer melts and polymer solutions *at equilibrium* we have encountered no problems with the method.[5,3] Nevertheless, it is always important to check—especially when tackling a new model system—that time averages converge to stationary values independent of the initial conditions used to start the simulations. We have not yet implemented a complex Langevin simulation of the above equations for nonequilibrium studies of inhomogeneous polymer solutions. One potential problem related to implementation of a such a simulation is that the choice of time scales $\tau_\epsilon, \tau_\mu \ll \tau_\sigma$ likely renders the equation set stiff. To minimize numerical difficulties associated with this stiffness, we suggest that $\tau_\epsilon \approx \tau_\mu$ be chosen as large as possible, but still small enough that the sensitivity of the σ and ρ dynamics to the values of these parameters is minimal.

C. Mean-field dynamics

It is evident that the above complex Langevin scheme, while very versatile and rich in physical content, will be computationally demanding to implement for large three-dimensional simulations. We thus consider options for simplifying the set of equations and thereby reducing the computational effort.

For dense systems in which mean-field theory is accurate, the fields μ and ϵ will fluctuate very close to their saddle point configurations, μ^* and ϵ^*, which prove to be purely imaginary. Under such conditions, we can ignore fluctuations in all fields by removing the noise sources in Eqs. (44)–(48). Moreover, Eqs. (47) and (48) can be replaced by the saddle point conditions $\delta H/\delta\mu = \delta H/\delta\epsilon = 0$, which adiabatically determine the two *real* saddle point fields $\bar{\mu}\equiv i\mu^*$, $\bar{\epsilon}\equiv i\epsilon^*$ as functionals of the instantaneous *real* density and stress fields, ρ and σ. Without noise sources, there is no need to retain the inertial terms in the momentum balance equations under typical conditions of low Reynolds number. Thus, the set of six complex stochastic equations reduce under these assumptions to a much simpler set of six real deterministic equations:

$$\frac{\partial}{\partial t}\rho = -\boldsymbol{\nabla}\cdot(\mathbf{v}_p\rho), \tag{54}$$

$$\frac{\partial}{\partial t}\sigma = -\boldsymbol{\nabla}\cdot(\mathbf{v}_p\sigma) + (\boldsymbol{\nabla}\mathbf{v}_p)^T\cdot\sigma + \sigma\cdot(\boldsymbol{\nabla}\mathbf{v}_p) - \frac{\rho}{\tau_\sigma}\frac{\delta H}{\delta\sigma}, \tag{55}$$

$$[\,\eta_s\nabla^2\mathbf{v} + \boldsymbol{\nabla}\cdot\Pi - \boldsymbol{\nabla}P\,]_\perp = 0, \tag{56}$$

$$\mathbf{w} = \zeta^{-1}\boldsymbol{\nabla}\cdot\Pi, \tag{57}$$

$$\frac{\delta H}{\delta \bar{\mu}} = 0, \tag{58}$$

$$\frac{\delta H}{\delta \bar{\epsilon}} = 0. \tag{59}$$

This equation set can be integrated forward in time to generate a dynamical trajectory for the retained structural fields ρ, σ, and the local flow $\mathbf{v}$. Equations (58) and (59) establish values of the conjugate mean fields $\bar{\mu}$ and $\bar{\epsilon}$ that are adiabatically slaved to the instantaneous density and stress fields and that can be used to evaluate the thermodynamic forces Π and $\delta H/\delta \sigma$ appearing in Eqs. (55)–(57). Equation (57) trivially establishes the relative flow between polymer and solvent, while Eq. (56) (along with the condition $\nabla \cdot \mathbf{v}=0$) can be solved to update the volume-averaged flow. Obviously, lacking thermal noise sources, Eqs. (54)–(59) cannot be used to study escape events from metastable states (e.g., nucleation).

This time-dependent variant of self-consistent mean-field theory is related to schemes for dynamics of inhomogeneous polymers that have been described by a number of authors, including Hasegawa and Doi,[30] Kawakatsu,[17] Yeung and Shi,[31] Reister *et al.*,[32] and most extensively by Fraaije and co-workers.[19,37–39] Unlike Hasegawa and Doi, Kawakatsu, Yeung and Shi, and Reister *et al.*, our formulation incorporates viscoelastic, multiphase flow in addition to diffusive mass transport. Equations (54)–(59) can thus describe phenomena such as Rayleigh instabilities associated with flows driven by interfacial and elastic stresses. The formalism of Fraaije and co-workers, often referred to as dynamic density functional theory, has been extended to approximately capture Stokesian hydrodynamic effects[38] and an appropriate volume-averaged stress operator has been identified.[37] A scheme for approximately incorporating viscoelastic effects has also been devised,[39] but it does not allow for inhomogeneous flows and does not properly embed the stress–concentration couplings that are known to be important in sheared polymer solutions. Finally, we note that our formalism contains the appropriate stress gradient terms that are necessary to produce the theoretically predicted slip phenomena at polymer–polymer interfaces.[40,41] In summary, we believe that Eqs. (54)–(59) provide an important extension of earlier mean-field approaches to the dynamics of inhomogeneous, unentangled polymers.

Further approximations (beyond the mean-field approximation) can be invoked to simplify Eqs. (54)–(59) for either analytical calculations or numerical simulations. One obvious target is to develop approximate analytical expressions for the functional $Q[i\mu, i\epsilon]$, thus avoiding the numerical solution of Eq. (11). This can be done in a variety of ways, but we comment here on two specific methods. The first method is to treat the gradient terms on the RHS of Eq. (11) as a perturbation and develop a long-wavelength expansion of q (and hence Q) in powers of gradients of the fields μ and ϵ. This gradient expansion was first demonstrated by Tang and Freed[23] (using a different approach) and is most applicable for systems in which the spatial inhomogeneities have

characteristic scales exceeding the radius of gyration of a polymer. The second method is to develop a perturbation expansion in the amplitudes of the μ and ϵ fields. This approach is implemented by instead viewing the first two terms on the RHS of Eq. (11) as a perturbation. The resulting (random phase approximation) expansion is closely related to that introduced by Leibler[42] in his treatment of weakly inhomogeneous block copolymer melts.

IV. SUMMARY AND OUTLOOK

In the present paper, we have shown how exact thermodynamic forces of a microscopic model of polymer solutions can be embedded into a complex Langevin dynamics version of the two-fluid model. We believe that this formalism will prove to be an excellent starting point for carrying out field-theoretic computer simulations of inhomogeneous polymer solutions out of equilibrium, such as polymer solutions undergoing spinodal decomposition or nucleation and growth, with or without imposed flow fields. Our method recovers the exact equilibrium properties of the starting polymer model and can be implemented without invoking the mean-field approximation. Moreover, it is faithful to the conservation laws, symmetries, and postulates of irreversible thermodynamics. We expect the field-theoretic simulation method to be most advantaged over more conventional "particle-based" computer simulation methods at higher polymer concentrations and for charged systems (polyelectrolytes), although this remains to be demonstrated. Finally, while elaborated here only for homopolymer solutions, the formalism can be easily extended to study the dynamics and rheology of multicomponent polymer solutions, polymer blends, and block and graft copolymer solutions and alloys.

One clear weakness of the two-fluid model is that entanglement effects are incorporated phenomenologically by amplification of the local friction coefficient ζ by appropriate factors of N/N_e.[12] This ignores the nonlocal, anisotropic nature of the reptation process and generates only local contributions to the various Onsager couplings. A more satisfactory (but tedious) approach for highly entangled solutions and melts would be to adapt the projection operator formalism of Kawasaki and Sekimoto[16] to include both density and stress as retained slow variables.

In the near future, we hope to report on extensions of the present formalism to treat other types of inhomogeneous polymer systems (including polyelectrolytes) and on implementations of the formalism to carry out field-theoretic computer simulations on a wide variety of systems. We are particularly interested in applying the method to reactive blending processes,[43] where the simultaneous action of phase separation, emulsification, convection, and diffusion are capable of producing exquisite and practically useful soft material structures.[44]

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J. Chem. Phys., Vol. 117, No. 14, 8 October 2002

Dynamics and rheology of inhomogeneous polymeric fluids   6819

APPENDIX A: DERIVATION OF EQ. (11)

In this Appendix, we sketch the derivation of the partial differential equation Eq. (11) satisfied by the chain propagator $q(\mathbf{r},s;[i\mu,i\epsilon])$. As is well known in the theory of quantum mechanics and stochastic processes,[25] path integrals such as Eq. (9) can be expressed in terms of the solution of Feynman–Kac type differential equations for propagators such as $q(\mathbf{r},s)$. (We subsequently drop the functional dependence of q on the conjugate fields to simplify the notation.) In the current context, $q(\mathbf{r},s)$ gives the probability density that a polymer chain of contour length s (and experiencing the inhomogeneous chemical potential and strain fields $i\mu$ and $i\epsilon$) has its end at position $\mathbf{r}$. To derive the relevant Feynman–Kac formula, we consider adding a differential increment of chain of contour length Δs. The Chapman–Kolmogorov equation of stochastic processes allows one to relate q of the incremented chain to that of the original chain:[45]

$$q(\mathbf{r},s+\Delta s)=\int d(\Delta \mathbf{r})T(\Delta \mathbf{r},\mathbf{r}-\Delta \mathbf{r})q(\mathbf{r}-\Delta \mathbf{r},s), \quad \text{(A1)}$$

where $\Delta \mathbf{r}$ is the three-dimensional displacement of the end of the incremented chain from the end of the original chain and $T(\Delta \mathbf{r},\mathbf{r})$ is the transition probability for a displacement of $\Delta \mathbf{r}$ starting from position $\mathbf{r}$. (This transition probability also depends on the contour step size Δs, but we suppress the Δs dependence for notational simplicity.) From the path integral of Eq. (9), it follows that

$$T(\Delta \mathbf{r},\mathbf{r})=\exp[-\tfrac{1}{2}\Delta \mathbf{r}^T \mathbf{C}(\mathbf{r})\Delta \mathbf{r}-i\Delta s\mu(\mathbf{r})]$$
$$\times\left(\int d(\Delta \mathbf{r})\exp(-\tfrac{1}{2}\Delta \mathbf{r}^T \mathbf{C}^0 \Delta \mathbf{r})\right)^{-1}, \quad \text{(A2)}$$

where the matrices $\mathbf{C}$ and $\mathbf{C}^0$ are defined by

$$C_{jk}(\mathbf{r})=\frac{3}{b^2\Delta s}[\delta_{jk}+2i\epsilon_{jk}(\mathbf{r})], \quad \text{(A3)}$$

$$C^0_{jk}(\mathbf{r})=\frac{3}{b^2\Delta s}\delta_{jk} \quad \text{(A4)}$$

and the superscript T denotes the transpose of a vector. The normalization of T evidently preserves the normalization of the original path integral, $Q[0,0]=1$.

Expanding the left-hand side of Eq. (A1) to order Δs and the right-hand side to order $(\Delta \mathbf{r})^2$ leads to

$$\frac{\partial}{\partial s}q=\frac{1}{\Delta s}(\langle 1\rangle-1)q+\frac{1}{2\Delta s}\nabla\nabla:[\langle \Delta \mathbf{r}\Delta \mathbf{r}\rangle q], \quad \text{(A5)}$$

where the averages denote displacement moments of the transition probability T, i.e., $\langle 1\rangle=\int d(\Delta \mathbf{r})T(\Delta \mathbf{r},\mathbf{r})$ and $\langle \Delta r_j\Delta r_k\rangle=\int d(\Delta \mathbf{r})T(\Delta \mathbf{r},\mathbf{r})\Delta r_j\Delta r_k$. These moments are easily evaluated from the Gaussian distribution, Eq. (A2). To order Δs, we find

$$\langle 1\rangle=\frac{1-i\Delta s\mu(\mathbf{r})}{\sqrt{\det[\mathbf{1}+2i\epsilon(\mathbf{r})]}}, \quad \text{(A6)}$$

$$\langle \Delta \mathbf{r}\Delta \mathbf{r}\rangle=\frac{b^2\Delta s}{3}\mathbf{m}(\mathbf{r};[i\epsilon]), \quad \text{(A7)}$$

where $\mathbf{m}(\mathbf{r};[i\epsilon])$ was defined in Eq. (12).

To leading order for small strains, i.e., strains $||\epsilon||\ll 1$ consistent with the use of the Gaussian chain model, the object appearing in Eq. (A5) simplifies to

$$\frac{1}{\Delta s}(\langle 1\rangle-1)\approx-\frac{i}{\Delta s}\text{tr }\epsilon(\mathbf{r})-i\mu(\mathbf{r}). \quad \text{(A8)}$$

The first term on the right-hand side is evidently singular for $\Delta s\to 0$. This singularity can be traced to our use of the continuous Gaussian chain model and is present even for a homogeneous strain ϵ. One approach to regularize this term is simply to set $\Delta s=1$. We prefer, however, to instead embed the exact corresponding expression from the discrete Gaussian chain model[1] subjected to a homogeneous strain. This choice leads to

$$\frac{1}{\Delta s}(\langle 1\rangle-1)\approx-\frac{1}{2}\text{tr ln}[\mathbf{1}+2i\epsilon(\mathbf{r})]-i\mu(\mathbf{r}). \quad \text{(A9)}$$

Equation (A9) is evidently consistent with Eq. (A8) to $O(\epsilon)$, once the latter is regularized by taking $\Delta s=1$. Substitution of Eqs. (A7) and (A9) into Eq. (A5) leads immediately to the partial differential equation for q reported in Eq. (11).

APPENDIX B: DERIVATION OF EQ. (20)

In this Appendix we sketch the derivation of Eq. (20), which provides an expression for how the auxiliary elastic stress operator can be constructed from a solution $q(\mathbf{r},s;[i\mu,i\epsilon])$ of the complex diffusion Eq. (11). We begin by explicitly forming the functional derivative in the defining equation for $\tilde{\sigma}$, Eq. (18). This leads to

$$\tilde{\sigma}_{jk}(\mathbf{r})=\frac{3n}{b^2Q}\int_0^N ds M_{jk}(\mathbf{r},s), \quad \text{(B1)}$$

where the tensor $\mathbf{M}$ is given by the following single-chain path integral:

$$M_{jk}(\mathbf{r},s)=\int \mathcal{D}[\mathbf{R}]\delta(\mathbf{r}-\mathbf{R}(s))\frac{dR_j}{ds}\frac{dR_k}{ds}\exp[-U_0-U_2]$$
$$\times\left(\int \mathcal{D}[\mathbf{R}]\exp[-U_0]\right)^{-1}. \quad \text{(B2)}$$

The elastic energy $U_0[\mathbf{R}]$ is given by Eq. (1), while $U_2[\mathbf{R}]$ denotes the interaction energy of the polymer with the chemical potential and strain fields:

$$U_2[\mathbf{R}]=\int_0^N ds\left[i\mu(\mathbf{R}(s))+\frac{3i}{b^2}\frac{d\mathbf{R}}{ds}\frac{d\mathbf{R}}{ds}:\epsilon(\mathbf{R}(s))\right]. \quad \text{(B3)}$$

By factorizing the path integral (B2) at $\mathbf{r}+\Delta \mathbf{r}$ and discretizing the chain segment from s to $s+\Delta s$, we find that $\mathbf{M}$ can be reexpressed as

$$M_{jk}(\mathbf{r},s)=\frac{1}{(\Delta s)^2V}\int d(\Delta \mathbf{r})q(\mathbf{r}+\Delta \mathbf{r},N-s-\Delta s)$$
$$\times q(\mathbf{r},s)T(\Delta \mathbf{r},\mathbf{r})\Delta r_j\Delta r_k, \quad \text{(B4)}$$

where $T(\Delta \mathbf{r}, \mathbf{r})$ is the transition probability of Eq. (A2). The next step is to expand the factor $q(\mathbf{r}+\Delta \mathbf{r}, N-s-\Delta s)$ in a Taylor series to second order in $\Delta \mathbf{r}$ and to first order in Δs. This generates a number of terms involving displacement moments of the transition probability T, such as those already evaluated in Eqs. (A6) and (A7). Here we require the fourth moment $\langle \Delta r_j \Delta r_k \Delta r_l \Delta r_m \rangle$, but this can be simply expressed in terms of second moments by invoking Wick's theorem:

$$\langle \Delta r_j \Delta r_k \Delta r_l \Delta r_m \rangle = \langle \Delta r_j \Delta r_k \rangle \langle \Delta r_l \Delta r_m \rangle + \langle \Delta r_j \Delta r_l \rangle$$
$$\times \langle \Delta r_k \Delta r_m \rangle + \langle \Delta r_j \Delta r_m \rangle \langle \Delta r_k \Delta r_l \rangle. \tag{B5}$$

The last step is simply to collect all the terms in $\mathbf{M}$ and substitute these into Eq. (B1) for the stress operator. We obtain

$$\tilde{\sigma}_{jk}(\mathbf{r},[i\mu,i\epsilon]) = \frac{1}{\Delta s}\tilde{\rho}(\mathbf{r},[i\mu,i\epsilon])[\delta_{jk}-2i\epsilon_{jk}(\mathbf{r})] - \delta_{jk}\frac{b^2}{6}\tilde{\rho}(\mathbf{r},[i\mu,i\epsilon])\boldsymbol{\nabla}\boldsymbol{\nabla}:\mathbf{m}(\mathbf{r}) - \delta_{jk}\frac{nb^2}{3VQ}[\nabla_l m_{lp}(\mathbf{r})]$$
$$\times \int_0^N ds\ q(\mathbf{r},s)\nabla_p q(\mathbf{r},N-s) + \frac{nb^2}{3VQ}m_{jl}(\mathbf{r})m_{kp}(\mathbf{r})\int_0^N ds\, q(\mathbf{r},s)\nabla_l\nabla_p q(\mathbf{r},N-s) \tag{B6}$$

where we have only retained terms up to $O(\epsilon)$, consistent with our small strain assumption. Finally, we note the singularity of the first term for $\Delta s \to 0$, similar to that encountered in Appendix A [cf. Eq. (A8)]. This is again associated with the use of the continuous Gaussian chain; a regularization consistent with that used to derive Eq. (11) (see Appendix A) corresponds to the choice of $\Delta s = 1$. With this simple change in Eq. (B6), Eq. (20) is immediately obtained.

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