Hydrodynamic theories for mixtures of polymers and rodlike liquid crystalline polymers

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We develop a hydrodynamic theory for flows of incompressible blends of flexible polymers and rodlike nematic polymers (RNPs) or rodlike nematic liquid crystal polymers (RNLCPs) extending the thermodynamical theory of Muratov and E [J. Chem. Phys. **116**, 4723 (2002)] for phase separation kinetics of the blend. We model the flexible polymer molecules in the polymer matrix as Rouse chains and assume the translational diffusion of the molecules is predominantly through the volume fraction of the flexible polymer and the molecules of rodlike nematic liquid crystal polymers. We then (i) derive the translational flux for the rodlike nematic liquid crystal polymers to ensure the incompressibility constraint; (ii) derive the elastic stress tensor, accounting for the contribution from both the rodlike nematic polymer and the flexible polymer matrix, as well as the extra elastic body force due to the nonlocal intermolecular potential for long range molecular interaction; (iii) show that the theory obeys positive entropy production and thereby satisfies the second law of thermodynamics. By applying the gradient expansion technique on the number density function of RNLCPs, we present an approximate, weakly nonlocal theory in differential form in which the intermolecular potential is given by gradients of the number density function of the RNLCP and the volume fraction of the flexible polymer. In the approximate theory, the elastic stress is augmented by an extra stress tensor due to the spatial convection of the macroscopic material point and long range interaction, whose divergence yields the analogous extra elastic body force with respect to the nonlocal intermolecular potential. Finally, we compare the model in steady simple shear with the Doi theory for bulk monodomains of rodlike nematic polymers.

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I. INTRODUCTION

Blends consisting of flexible polymers with rodlike nematic liquid crystal polymers (RNLCPs) or simply rodlike nematic polymers have many material applications due to their potentially ultrahigh modulus and stiffness. Polymer-dispersed liquid crystals and polymer-stabilized small molecule liquid crystals have been used in electro-optic devices such as liquid crystal display devices, light shutters/switches, and protective goggles [1]. Blends of polymers and rodlike nematic liquid crystalline polymers often exhibit remarkable mechanical, electrical and thermal properties making them ideal high-performance materials in industrial and military applications [2,3]. Blends are also relatively cheap to make.

Given the promising applications of blends of flexible polymers and rodlike nematic liquid crystalline polymers, a thorough understanding of their mesophase dynamics, morphology development and mesoscopic structure evolution, and the full spectrum of rheological behavior in processing conditions becomes important. Yet theoretical studies of these aspects of the polymer blends are sparse. Liu and Fredrickson developed a mean field thermodynamic theory to study phase separation kinetics focusing on low frequency and long wave behavior [4]. Muratov and E proposed a thermodynamic theory based on a kinetic theory approach for the incompressible mixture of flexible polymers and rodlike liquid crystalline polymers neglecting the details of the flexible polymer chain [5]. They also investigated the phase separation kinetics with an approximate theory employing a gradient expansion of the density function of the rodlike liquid crystalline polymer. They identified various transitions leading to phase separation including a microphase separation transition. In both of these theories, the detailed conformational dynamics of the flexible polymers are ignored. However, the conformational dynamics of flexible polymers could be instrumental for a faithful hydrodynamic theory, especially, in the dilute RNLCP regime typical of materials applications. This paper addresses the local conformational dynamics of both the flexible polymer and RNLCP in a hydrodynamic theory for the blend.

This paper aims at the following.

1) Introducing an additional probability density function for the flexible polymer chains to account for the local conformational dynamics of the polymer at the molecular level.

2) Extending the Muratov-E kinetic theory to account for added flexible chain dynamics and reenforce the incompressibility constraint.

3) Coupling the kinetic (Smoluchowski) equation to the momentum transport process by deriving the stress and body force expressions accounting for the contribution from both the RNLCP and the flexible polymer chain.

4) Demonstrating positive entropy production and thereby the second law of thermodynamics under a suitable condition on the mobility matrix in the kinetic theory.

We then approximate the bulk free energy functional using a gradient expansion scheme in physical space, arriving

at an approximate theory with potentials of differential form, which captures mesoscale structures much larger than the molecular scale. We remark that this approach builds upon the hydrodynamic theories for solutions of rodlike liquid crystalline polymers of the Doi type, see for example [6–8]. In a series of papers involving detailed force calculations [9–11], Dhont and Briels developed a hydrodynamic theory for suspensions of arbitrary shape and later limited to long and thin rigid rods in viscous solvent extending the early work of Batchelor's on volume averaging techniques. This theory takes into account the hydrodynamic interaction of neighboring beads that constitute the rigid rod and distribution inhomogeneity of the rigid suspensions and is expected to be applicable to flows of large density variation and velocity gradients, complimenting the Doi kinetic theory for solutions of rodlike liquid crystals. Viscoelasticity of the new theory in simple flows is examined as well.

In kinetic theories for mixtures, one may introduce a statistical weight or its normalized counterpart, the probability density function, for each component. However, they are not independent if the mixture is incompressible. Since the incompressibility condition is a geometric constraint, it is normally given through the volume fractions. In Muratov-E theory for binary mixtures of flexible polymer and RNLCPs, the volume fractions can be interpreted as the quantity proportional to the zeroth moment of the statistical weight for each component at the macroscopic level. We also recognize the fact that the incompressibility constraint is closely related to the translational flux for each component, but has nothing to do with the rotary flux of the RNLCP. This motivates us to introduce the conformational dynamics for the flexible polymer locally so that it will not affect the incompressibility constraint imposed at the macroscopic level. Specifically, we introduce a statistical weight for the flexible polymer matrix $\Theta(\mathbf{x},\{\mathbf{R}\}_i,t)$, where $\mathbf{x}$ is the location of the material point, t is time, and $\{\mathbf{R}\}_i=(\mathbf{R}_1,\ldots,\mathbf{R}_n)$ describes the conformation of the flexible polymer chain modeled as a Rouse chain, i.e., a bead-spring chain [6,18]. We assume Θ can be separated into a product of two functions, $\phi(\mathbf{x},t)$ and $\theta(\{\mathbf{R}\}_i,t)$, where θ is a probability density function for the orientation of the Rouse chain (whose norm is 1) and ϕ is the volume fraction of the polymer per unit volume at the macroscopic level. The time evolution of θ is given by the Rouse dynamics while that of ϕ follows the extended Flory-Huggins approach [5]. Since the added conformational dynamics is local, it would not affect the incompressibility constraint macroscopically. It does however add a detailed conformational contribution of the flexible polymer to the elastic stress. In principle, FENE, FENE-p, and Giesekus models can all be cast in this form of the kinetic theory.

The rest of the paper is organized into four sections. First, we develop the theory with a nonlocal intermolecular potential accounting for Brownian motion, excluded volume effects, and long range molecular interactions. We show that the theory satisfies the second law of thermodynamics under a suitable condition for the mobility matrix. We then focus on development of the approximate, weakly nonlocal theory using a gradient expansion scheme for the density function of the RNLCP. Finally, we compare the current theory with that of Doi for rodlike nematic polymers in sheared monodomains.

II. HYDRODYNAMIC THEORY WITH A NONLOCAL INTERMOLECULAR POTENTIAL

We first introduce the relevant statistical weights for the rodlike nematic liquid crystal polymers (RNLCPs) and the flexible polymers in the mixture, respectively, and devise the free energy of the material system using the statistical weights. Then, we enforce the incompressibility condition at the macroscopic level to derive a constraint for the statistical weights. In this manner, the statistical weight for the flexible polymer can be eliminated so that the Smoluchowski equation for the RNLCP statistical weight, called the number density per unit volume, can be derived, providing a description of the orientational distribution of RNLCPs as well as spatial distribution of the entire material system. The elastic stress tensor is derived through an extended virtual work principle, and the constitutive viscous stress is derived following the Doi-Edwards approach [6].

For incompressible mixtures of flexible polymers and rodlike nematic liquid crystal polymers, we introduce two key variables: (i) the number density of RNLCPs per unit volume $f(\mathbf{x},\mathbf{m},t)$ at $(\mathbf{x},t)$ with molecular orientation axis $\mathbf{m}$; and, (ii) another statistical weight proportional to the number density of flexible polymers per unit volume $\Theta(\mathbf{x},\{\mathbf{R}\}_\mathbf{i},\mathbf{t})$ at $(\mathbf{x},t)$ with the chain conformation $\{\mathbf{R}\}_i=(\mathbf{R}_1,\ldots,\mathbf{R}_n)$. A Rouse chain (bead-spring chain) is used for the flexible polymer with $\mathbf{R}_i$ denoting the location of the ith bead. We normalize Θ so that

$$\phi(\mathbf{x},t)=\int \Theta(\mathbf{x},\{\mathbf{R}\}_\mathbf{i},\mathbf{t})\mathbf{dR}_1\cdots\mathbf{dR}_\mathbf{n} \tag{1}$$

is the volume fraction of the flexible polymer at $(\mathbf{x},t)$. We further assume Θ is separable,

$$\Theta(\mathbf{x},\{\mathbf{R}\}_\mathbf{i},\mathbf{t})=\phi(\mathbf{x},\mathbf{t})\,\theta(\{\mathbf{R}\}_\mathbf{i},\mathbf{t}), \tag{2}$$

where $\theta(\{\mathbf{R}\}_\mathbf{i},\mathbf{t})$ is the probability density function for the Rouse chain, i.e.,

$$\int \theta(\{\mathbf{R}\}_i,t)d\mathbf{R}_1\cdots d\mathbf{R}_n=1. \tag{3}$$

According to the definition of f,

$$\Phi(\mathbf{x},t)=\int_{\|\mathbf{m}\|=1} f(\mathbf{m},\mathbf{x},t)d\mathbf{m} \tag{4}$$

defines the number density of RNLCPs at location $\mathbf{x}$ and time t. We denote the emsemble average with respect to the probability density function θ by

$$\langle\langle(\cdot)\rangle\rangle=\int(\cdot)\,\theta(\{\mathbf{R}\}_\mathbf{i},\mathbf{t})\mathbf{dR}_1\cdots\mathbf{dR}_\mathbf{n} \tag{5}$$

and the ensemble average with respect to the number density function f by

$$\langle(\cdot)\rangle=\int_{\|\mathbf{m}\|=1}(\cdot)f(\mathbf{x},\mathbf{m},t)d\mathbf{m}. \tag{6}$$

We propose a free energy functional for the mixture of polymers and rodlike nematic polymers consisting of four

parts: free energy associated with the Brownian motion and excluded volume interaction among the RNLCP molecules, free energy for flexible polymers based on the Flory-Huggins theory with a conformational entropy of the polymer chain included, the elastic potential for Rouse chains, and the free energy due to the contact interaction between the RNLCP and flexible polymer molecules [5]. The free energy presented here is more general than the one used in [5] in that the RNLCP molecular shape information can be naturally built in through the shape characteristic function $H(\mathbf{m},\mathbf{x})$ defined below, and the range of molecular interaction can be readily accounted for through a second kernel function $B(\mathbf{m},\mathbf{m}',\mathbf{x})$. It thus allows more general molecular configurations and long range interactions to be modeled within the framework of the theory. The excluded volume interaction for the flexible polymers can be easily accounted for by adding an additional excluded volume potential for Rouse chains in the free energy [6], which has a negligible contribution to the elastic stress. For the sake of simplicity, we neglect this effect in the current derivation. In the following, we assume the RNLCP molecules are monodispersed rigid rods, the flexible polymer matrix consists of Rouse chains of uniform molecular weight, and the effects of gelation, polydispersity and polymerization of the flexible polymers are ignored.

A. Free energy

Let $A[f]$ denote the free energy of the mixture in material volume Ω,

$$A[f] = F_{lc} + F_{poly} + F_{polyrouse} + F_{int}, \tag{7}$$

where F_{lc} is the free energy associated with the RNLCPs, F_{poly} is the entropic free energy associated with the flexible polymers, $F_{polyrouse}$ is the free energy associated with the conformational change of the flexible polymer modelled as a Rouse chain, and F_{int} is the free energy due to the polymer-LCP interaction. Specifically,

$$F_{lc} = kT\int_{\Omega}\int_{\|\mathbf{m}\|=1}\Big(f(\mathbf{m},\mathbf{x},t)\ln f(\mathbf{m},\mathbf{x},t) - f(\mathbf{m},\mathbf{x},t) + \tfrac{1}{2}U(\mathbf{m},\mathbf{x},t)f(\mathbf{m},\mathbf{x},t)\Big)d\mathbf{m}\,d\mathbf{x},$$

$$U(\mathbf{m},\mathbf{x},t) = \int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'') \times f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}', \tag{8}$$

where $f=f(\mathbf{m},\mathbf{x},t)$ is the number density of the rodlike liquid crystal polymer in molecular direction $\mathbf{m}$ at location $\mathbf{x}$ and time t, k is the Boltzmann constant, T is the absolute temperature, $B(\mathbf{m},\mathbf{m}',\mathbf{x})$ and $H(\mathbf{m},\mathbf{x})$ are defined below, and Ω is the domain that the blend system occupies;

$$F_{poly} = kT\int_{\Omega}\left(\frac{b^2}{2}\|\nabla\phi(\mathbf{x},t)\|^2 + \frac{\phi}{n}\ln\phi(\mathbf{x},t) + \chi_p\phi^2(\mathbf{x},t)\right)d\mathbf{x}, \tag{9}$$

where the gradient term is used for penalizing the spatial inhomogeneity of the polymer representing the conformational entropy, b is the coherence length measuring the strength of the conformational entropy, χ_p is the interaction parameter for polymers, n is the polymerization index;

$$F_{polyrouse} = kT\gamma\int_{\Omega}\phi(\mathbf{x},t)\int\Bigg[\theta(\{\mathbf{R}\}_\mathbf{i},\mathbf{t})\ln\theta(\{\mathbf{R}\}_\mathbf{i},\mathbf{t}) + \xi\sum_{k=2}^{n}\|\mathbf{R}_k-\mathbf{R}_{k-1}\|^2\theta(\{\mathbf{R}_i\},t)\Bigg](d\mathbf{R}_i)d\mathbf{x}, \tag{10}$$

where ξ is the spring constant for the Rouse chain and γ is a parameter of dimension of 1/volume ($1/\gamma$ is proportional to the effective volume of a flexible polymer molecule);

$$F_{int} = kT\chi\int_{\Omega^2}\int_{\|\mathbf{m}\|=1}\phi(\mathbf{x}',t)H(\mathbf{m},\mathbf{x}-\mathbf{x}')f(\mathbf{m},\mathbf{x},t)d\mathbf{x}'d\mathbf{m}\,d\mathbf{x}, \tag{11}$$

where χ is the polymer-LCP interaction parameter [6,5]. Here, we assume molecules of flexible polymers interact with segments of the LCP molecule. We note that, when the mixture is spatially homogeneous, our free energy expression for the LCP alone (F_{lc}) reduces to the one calculated from the partition theorem by Doi and Edwards in [6]. The function

$$B(\mathbf{m},\mathbf{m}',\mathbf{x}) = \begin{cases}\dfrac{C}{v(B)}\|\mathbf{m}\times\mathbf{m}'\|, & \text{if } \mathbf{x}\in B(0,R),\\ 0, & \text{otherwise,}\end{cases} \tag{12}$$

defines the excluded volume and the range of molecular interaction with $B(0,R)$ a ball of radius R in $\mathbf{R}^3$, $v(B)$ is the volume of the ball. $C\|\mathbf{m}\times\mathbf{m}'\|$ is the excluded volume, where $C=2L^2r_c$ with L the length of the rodlike molecule and r_c its cross-sectional diameter. Of course, a more sophisticated range of interaction can be constructed depending on the level of modeling desired. In this paper, we adopt a spherical domain for long range, isotropic interactions in space, where

$$H(\mathbf{m},\mathbf{x}) = \begin{cases}\dfrac{1}{v(S(0))}, & \mathbf{x}\in S(0),\\ 0, & \text{otherwise,}\end{cases} \tag{13}$$

is the shape characteristic function of the LCP molecule, $S(0)$ is the domain occupied by the molecule with its center of mass at the origin, $v(S(0))$ denotes the volume of $S(0)$. This shape function allows us to incorporate the molecular configuration into the intermolecular potential extending the applicability of the theory to more complex shapes of LCP molecules. For RNLCPs, H is the normalized characteristic function of a cylinder with height L and cross-sectional diameter r_c.

B. Incompressibility

We treat the polymer-LCP mixture as incompressible. Let $\bar{V}=v(S(0))$ be the volume of each individual LCP molecule. Then, the incompressibility condition states that the volume

fractions of the two components add up to unity:

$$\phi(\mathbf{x},t) + \bar{V}\Phi(\mathbf{x},t) = 1. \tag{14}$$

That is, the mixture is filled with polymers and LCPs without any free space. This constraint links the fundamental dynamical variable $\Theta(\mathbf{x},\{\mathbf{R}\}_\mathbf{i},\mathbf{t})$ to $f(\mathbf{m},\mathbf{x},t)$ and affects the kinetics of the mixture.

C. Kinetics

For translational diffusion of the LCP molecules, we adopt the approach of Doi and Edwards [6], allowing motions along the direction of the LCP molecular orientation as well as its transverse directions with distinct diffusivities $D_\parallel$ and $D_\perp$, respectively [6,12]. While the mixture is incompressible, the incompressibility condition imposes a constraint on the transport equations for both ϕ and f such that the transport equation of ϕ can be derived from that of f. E and Palffy-Muhoray noted that the divergence of the translational flux of ϕ and Φ must add up to zero in order to maintain constraint (14). They then showed that their flux condition is equivalent to modifying each flux by an additional pressurelike flux to accommodate the incompressibility constraint (14) [13]. DeGennes handled the incompressibility constraint by requiring the fluxes add up to zero at any material point [14], which is a special case of the E-Palffy-Muhoray condition [13]. Although the E-Palffy-Muhoray condition is more general, the pressurelike flux is very difficult to obtain analytically. As a compromise, we adopt Muratov and E's approach, where a Lagrange multiplier is used [5]; i.e., we propose modified translational fluxes for the RNLCP and flexible polymer, respectively, as follows [5]:

$$kT\mathbf{j}_f = -[D_\parallel \mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm})]\cdot f(\nabla\mu_{lc} - \bar{V}\mathbf{h}),$$

$$kT\mathbf{j}_\phi = -D_\phi\phi(\nabla\mu_\phi - \mathbf{h}), \tag{15}$$

where $D_\parallel$ and $D_\perp$ are the translational diffusivity in the direction of $\mathbf{m}$ and its transverse directions, respectively; μ_{lc} and μ_ϕ are the "extended" chemical potential of the LCP and the flexible polymer, respectively, i.e., they are the variations of the free energy with respect to f and ϕ while holding ϕ and f constant, respectively, and given by

$$\mu_{lc} = \frac{\delta A}{\delta f} = kT\left(\ln f + \tfrac{1}{2}(U+U_2)\right) + \chi kT\int_\Omega \phi(\mathbf{x}',t)H(\mathbf{m},\mathbf{x}-\mathbf{x}')d\mathbf{x}',$$

$$\mu_\phi = \frac{\delta A}{\delta\phi} = kT\left(\frac{1}{n}(\ln\phi+1) + 2\chi_p\phi - b^2\Delta\phi + \gamma\left\langle\left\langle \ln\theta + \xi\sum_{k=2}^{n}\|\mathbf{R}_k - \mathbf{R}_{k-1}\|^2\right\rangle\right\rangle\right) + \chi kT\int_\Omega\int_{\|\mathbf{m}\|=1} H(\mathbf{m},\mathbf{x}'-\mathbf{x})f(\mathbf{m},\mathbf{x}',t)d\mathbf{x}'d\mathbf{m},$$

$$U_2(\mathbf{m},\mathbf{x},t) = \int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m}',\mathbf{m},\mathbf{x}''-\mathbf{x}')H(\mathbf{m},\mathbf{x}'-\mathbf{x}) \times f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}', \tag{16}$$

$U_e = \frac{1}{2}(U+U_2)$ is the effective intermolecular potential for RNLCPs; $\mathbf{h}$ is a spatial flux (a Lagrangian multiplier) to be determined by the flux condition defined below to ensure the incompressibility condition (14). We impose the flux condition consistent with the incompressibility constraint (14) as follows [5]

$$\mathbf{j}_\phi + \bar{V}\int_{\|\mathbf{m}\|=1}\mathbf{j}_f d\mathbf{m} = \mathbf{0}. \tag{17}$$

This leads to

$$\mathbf{h} = \Lambda^{-1}\cdot\left[D_\phi\phi\nabla\mu_\phi + \bar{V}\int_{\|\mathbf{m}\|=1}(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm})) \times f(\mathbf{m},\mathbf{x},t)\nabla\mu_{lc}d\mathbf{m}\right],$$

$$\Lambda = D_\phi\phi\mathbf{I} + \bar{V}^2\int_{\|\mathbf{m}\|=1}(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))f(\mathbf{m},\mathbf{x},t)d\mathbf{m}. \tag{18}$$

The modified fluxes are then given by

$$kT\mathbf{j}_f = -(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\Lambda^{-1}\cdot f[D_\phi\phi\nabla\mu + \bar{V}^2[\langle(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\rangle\nabla\mu_{lc} - \langle(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\nabla\mu_{lc}\rangle]],$$

$$kT\mathbf{j}_\phi = D_\phi\Phi\Lambda^{-1}\left[\bar{V}\int_{\|\mathbf{m}\|=1}(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm})) \times f\cdot\nabla\mu d\mathbf{m}\right], \tag{19}$$

where

$$\mu = \mu_{lc} - \bar{V}\mu_\phi \tag{20}$$

is the variation of the free energy with respect to f subject to the incompressibility constraint (17).

Notice that μ_ϕ is independent of the orientation variable $\mathbf{m}$, so the last two terms in flux $\mathbf{j}_f$ can be written as

$$\bar{V}^2\langle(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\rangle\cdot\nabla\mu_{lc} - \langle(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu_{lc}\rangle = \bar{V}^2\langle(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\rangle\cdot\nabla\mu - \langle(D_\parallel\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle. \tag{21}$$

So, the modified flux for f can be further simplified into

$$kT\mathbf{j}_f = -(D_\parallel \mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\cdot f[\nabla\mu - \bar{V}^2\Lambda^{-1}\cdot\langle(D_\parallel \mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm}))\nabla\mu\rangle]. \quad (22)$$

We remark that the second term in (22) is a density averaged restraining force which serves to maintain the incompressibility constraint.

In addition to the translational fluxes, there exists a rotary flux in the configurational space $\mathbf{m}\in S^2$ for the RNLCP given by

$$kT\mathbf{j}^r_{\mathbf{m}} = -fD_r(\mathbf{m})\mathcal{R}\mu, \quad (23)$$

where $D_r(\mathbf{m})$ is the rotary diffusivity and $\mathcal{R}=\mathbf{m}\times\partial/\partial\mathbf{m}$ is the rotational gradient operator [6]. We note that this rotary flux does not contribute to the spatial flux on average since

$$\int_{\|\mathbf{m}\|=1}\mathcal{R}\cdot\mathbf{j}^r_{\mathbf{m}}d\mathbf{m} = 0. \quad (24)$$

Together with the spatial flux, they constitute the total flux in phase space $(\mathbf{x},\mathbf{m})\in R^3\times S^2$ for the RNLCP. Analogously, the flux of the flexible polymer in the conformational space $\{\mathbf{R}\}_\mathbf{i}$ is also independent of the corresponding translational flux. The chemical potential for the local Rouse chain can be identified as

$$\mu_\theta = \gamma kT\left[\ln\theta + 1 + \xi\sum_{k=2}^{n}\|\mathbf{R}_k - \mathbf{R}_{k-1}\|^2\right]. \quad (25)$$

The conformational flux of the flexible polymer is given by

$$(\mathbf{j}_\theta)_i = -\mathbf{H}_{ij}\cdot\frac{\partial}{\partial\mathbf{R}_j}\mu_\theta, \quad i=1,\ldots,n, \quad (26)$$

where $\mathbf{H}_{ij}$ is the mobility matrix for the Rouse chain [6].

D. Smoluchowski equation

Given the above fluxes due to translational and rotary diffusion and taking into account the spatial convection as well as the rotary convection [6], we follow Doi and Edwards to arrive at the Smoluchowski equation for $f(\mathbf{m},\mathbf{x},t)$ as follows:

$$\frac{df}{dt} = -\boldsymbol{\nabla}\cdot(\mathbf{j}_f) + \mathcal{R}\cdot\left(\frac{D_r(\mathbf{m})}{kT}f\mathcal{R}\mu\right) - \mathcal{R}\cdot(\mathbf{m}\times\dot{\mathbf{m}}f),$$

$$\dot{\mathbf{m}} = K\cdot\mathbf{m} - K{:}\mathbf{mmm}, \quad (27)$$

where $K=\nabla\mathbf{v}$ is the velocity gradient tensor and $d/dt=\partial/\partial t+\mathbf{v}\cdot\boldsymbol{\nabla}$ is the material derivative. It is an integro-differential equation for f. The time evolution equation for the volume fraction ϕ is given by

$$\frac{d}{dt}\phi = -\boldsymbol{\nabla}\cdot\mathbf{j}_\phi, \quad (28)$$

which can also be derived from the Smoluchowski equation for f through averaging. The time evolution equation for θ is

$$\frac{d}{dt}\theta = -\frac{\partial}{\partial\mathbf{R}_i}\cdot([\mathbf{K}-(1-a)\mathbf{D}]\cdot\mathbf{R}_i\theta) + \frac{\partial}{\partial\mathbf{R}_i}\cdot\mathbf{H}_{ij}\cdot\left(\frac{\partial}{\partial\mathbf{R}_j}\mu_\theta\theta\right), \quad (29)$$

where $-1\leqslant a\leqslant 1$ is a rate parameter describing the extent of the nonaffine motion, $H_{ij}=(1/\zeta_p)\mathbf{I}$ is the mobility matrix for the Rouse model and ζ_p is a friction coefficient for the Rouse chain [6]. In order to couple the kinetic equation for the momentum transport process in the macroscopic flow, we need the stress and body force expression for the mixture [15].

E. Stress tensors and the elastic body force

The extra stress is given by two parts, the viscous stress τ_v and the elastic stress τ_e:

$$\tau = \tau_v + \tau_e. \quad (30)$$

Here we consider two sources for the viscous stress. There must be a zero-strain-rate viscosity while the mixture is isotropic. We denote this as η_v. The viscous stress associated to this effect is denoted as $2\eta_v\mathbf{D}$. In addition, there is a viscous stress due to the friction between polymers and RNLCP molecules. Using the same argument as Doi and Edwards [6], we arrive at the viscous stress $2kT\zeta\mathbf{D}:\langle\mathbf{mmmm}\rangle$, where the friction coefficient ζ is approximated by a linear function of the polymer volume fraction ϕ (embeded in the ensemble average $\langle\ \rangle$) to ensure the viscous stress vanishes in the region where RNLCPs are depleted. The overall viscous stress is therefore given by

$$\tau_v = 2\eta_v D + 2kT\zeta\mathbf{D}{:}\langle\mathbf{mmmm}\rangle. \quad (31)$$

The elastic stress and extra elastic body force are derived through a virtual work principle [6]. Consider an infinitesimal displacement given by $\delta\mathbf{u}=\mathbf{v}\delta t$ corresponding to a deformation rate $\delta\epsilon=K\delta t$. The variation of the free energy (7) in response to the infinitesimal deformation and displacement is equal to the work done by a body force along the displacement and the stress with respect to the deformation rate:

$$\delta A = \int_\Omega[\delta\epsilon{:}\tau_e - \delta\mathbf{u}\cdot\mathbf{F}_e]d\mathbf{x}, \quad (32)$$

where F_e is the elastic body force induced by the long range interaction between the RNLCPs and polymer-RNLCP interaction. It follows from a long calculation summarized in Appendix A that

$$\mathbf{F}_e = -kT\left[\langle\nabla U_e\rangle + \chi\int_\Omega[\phi(\mathbf{x}',t)\langle\nabla H(\mathbf{m},\mathbf{x}-\mathbf{x}')\rangle + \phi(\mathbf{x},t)\langle\nabla H(\mathbf{m},\mathbf{x}'-\mathbf{x})\rangle]d\mathbf{x}\right], \quad (33)$$

where

$$\langle \nabla H(\mathbf{m}, \mathbf{x}-\mathbf{x}') \rangle = \int_{\|\mathbf{m}\|=1} \big(\nabla H(\mathbf{m}, \mathbf{x}-\mathbf{x}')\big) f(\mathbf{m}, \mathbf{x}, t) d\mathbf{m} \tag{34}$$

and

$$\tau_e = -\langle \mathbf{m} \times \mathcal{R}\mu_{lc}\mathbf{m} \rangle - kTb^2 \nabla \phi \nabla \phi + \phi \left\langle\!\!\left\langle \sum_{i=1}^{n} \frac{\partial \mu_\theta}{\partial \mathbf{R}_i} \mathbf{R}_i \right\rangle\!\!\right\rangle. \tag{35}$$

We note that

$$\sum_{i=1}^{n} \left\langle\!\!\left\langle \frac{\partial \mu_\theta}{\partial \mathbf{R}_i} \mathbf{R}_i \right\rangle\!\!\right\rangle = 2kT\gamma\xi \sum_{i=1}^{n-1} \langle\langle (\mathbf{R}_{i+1}-\mathbf{R}_i)(\mathbf{R}_{i+1}-\mathbf{R}_i) \rangle\rangle + \text{const} \times \mathbf{I}. \tag{36}$$

The total extra stress is then given by

$$\tau = 2\eta_v D + 2kT\zeta \mathbf{D}:\langle \mathbf{mmmm} \rangle - \langle \mathbf{m} \times \mathcal{R}\mu_{lc}\mathbf{m} \rangle - kTb^2 \nabla \phi \nabla \phi + 2\gamma kT\phi\xi \sum_{i=1}^{n-1} \langle\langle (\mathbf{R}_{i+1}-\mathbf{R}_i)(\mathbf{R}_{i+1}-\mathbf{R}_i) \rangle\rangle. \tag{37}$$

The elastic stress expression includes contributions from the RNLCP, the flexible polymer and the polymer-LCP interaction, some of which are nonlocal. We note that the expression for the elastic stress and the extra elastic body force are interrelated. If the body force can be written into a divergence of a second order tensor, the tensor can well be absorbed into the stress expression. Therefore a true elastic body force exists only when it cannot be identified with the divergence of a second order tensor.

The existence of the elastic body force is a consequence of the spatial convection of the RNLCPs and the nonlocal LCP-LCP as well as polymer-LCP interaction as shown in the derivation in Appendix A. When the long range interaction is allowed to affect different material points, the nonlocal potential exerts a macroscopic body force, part of which becomes the extra elastic body force and the other equals the divergence of the elastic stress. This is a generic phenomenon so long as the intermolecular potential is nonlocal in $\mathbf{R}^3$ [15].

Let ρ_p be the polymer density and ρ_{lc} the density of the RNLCP. The density of the mixture is given by

$$\rho = \rho_p \phi + \rho_{lcp} \bar{V} \Phi. \tag{38}$$

If $\rho_p = \rho_{lcp}$, the incompressibility constraint implies that

$$\dot{\rho} = 0. \tag{39}$$

The continuity equation

$$\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0 \tag{40}$$

implies the divergence-free condition on the velocity field

$$\nabla \cdot \mathbf{v} = 0. \tag{41}$$

Otherwise, the mass conservation (40) serves as a constraint for the flowing mixture system:

$$\nabla \cdot \mathbf{v} = -\dot{\overline{\ln \rho}}. \tag{42}$$

In this paper, we assume $\rho_p = \rho_{lcp}$ so that the continuity equation (41) holds. In general, the stress would have to be modified to reflect the constraint imposed by the continuity equation (40).

F. Governing equations

The Smoluchowski equation, the stress expression along with the elastic body force, continuity equation and the balance of linear momentum equation constitute the governing system of equations for flows of the polymer-LCP mixture. We summarize them in the following.

Continuity equation:

$$\frac{d}{dt}\rho + \rho \nabla \cdot \mathbf{v} = 0. \tag{43}$$

Balance of linear momentum:

$$\rho \dot{\mathbf{v}} = \nabla \cdot (-p\mathbf{I} + \tau) + \mathbf{F}_e + \rho \mathbf{g}, \tag{44}$$

where p is the static pressure and $\mathbf{g}$ is the external force per unit mass.

Smoluchowski equations or kinetic equations:

$$\frac{df}{dt} = -\nabla \cdot (\mathbf{j}_f) + \mathcal{R} \cdot \left(\frac{D_r(\mathbf{m})}{kT} f \mathcal{R}\mu \right) - \mathcal{R} \cdot (\mathbf{m} \times \dot{\mathbf{m}} f),$$

$$\dot{\mathbf{m}} = K \cdot \mathbf{m} - K:\mathbf{mmm},$$

$$\frac{d}{dt}\phi = -\nabla \cdot \mathbf{j}_\phi,$$

$$\frac{d}{dt}\theta = -\frac{\partial}{\partial \mathbf{R}_i} \cdot ([\mathbf{K} - (1-a)\mathbf{D}] \cdot \mathbf{R}_i \theta) + \frac{\partial}{\partial \mathbf{R}_i} \cdot \mathbf{H}_{ij} \cdot \left(\frac{\partial}{\partial \mathbf{R}_j} \mu_\theta \theta \right). \tag{45}$$

Stress constitutive equation:

$$\tau = 2\eta_v D + 2kT\zeta \mathbf{D}:\langle \mathbf{mmmm} \rangle - \langle \mathbf{m} \times \mathcal{R}\mu_{lc}\mathbf{m} \rangle - kTb^2 \nabla \phi \nabla \phi + 2\gamma kT\phi\xi \sum_{i=1}^{n-1} \langle\langle (\mathbf{R}_{i+1}-\mathbf{R}_i)(\mathbf{R}_{i+1}-\mathbf{R}_i) \rangle\rangle. \tag{46}$$

Body force constitutive equation:

$$\mathbf{F}_e = -kT \left[\langle \nabla U_e \rangle + \chi \int_\Omega [\phi(\mathbf{x}', t) \langle \nabla H(\mathbf{m}, \mathbf{x}-\mathbf{x}') \rangle + \phi(\mathbf{x}, t) \langle \nabla H(\mathbf{m}, \mathbf{x}'-\mathbf{x}) \rangle] d\mathbf{x}' \right]. \tag{47}$$

We next examine the dissipative property of the theory.

III. ENTROPY PRODUCTION AND ENERGY DISSIPATION

We denote the entropy of the mixture system in the control volume Ω by S. The entropy production of an isothermal system is given by [16]

$$
\begin{aligned}
T\dot{S} &= -\frac{d}{dt}\left[\int_\Omega \tfrac{1}{2}\rho \mathbf{v}\cdot\mathbf{v}d\mathbf{x} + A[f]\right] \\
&= -\int_\Omega (\nabla\cdot(-p\mathbf{I}+\tau_v+\tau_e)+\mathbf{F}_e)\cdot\mathbf{v}d\mathbf{x} - \int_\Omega \frac{d}{dt}A[f]d\mathbf{x} \\
&= \int_\Omega ((-p\mathbf{I}+\tau_v+\tau_e):\nabla\mathbf{v}-\mathbf{F}_e)\cdot\mathbf{v}d\mathbf{x} - \int_\Omega \frac{d}{dt}A[f]d\mathbf{x} \\
&= \int_\Omega \tau_v:\nabla\mathbf{v}d\mathbf{x} - \int_\Omega\int_{\|\mathbf{m}\|=1} \mu\frac{d^*}{dt}f(\mathbf{m},\mathbf{x},t)d\mathbf{m}\,d\mathbf{x} \\
&= \int_\Omega [2\eta_v\mathbf{D}:\mathbf{D} + 2kT\zeta\langle(\mathbf{mm}:\mathbf{D})^2\rangle]d\mathbf{x} + \frac{1}{kT}\int_\Omega \langle\nabla\mu\cdot(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm})) \\
&\quad\cdot[\nabla\mu - \bar{V}^2\Lambda^{-1}\cdot\langle(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle] + \mathcal{R}\mu\cdot D_r\mathcal{R}\mu\rangle d\mathbf{x} \\
&= \int_\Omega [2\eta_v\mathbf{D}:\mathbf{D} + 2kT\zeta\langle(\mathbf{mm}:\mathbf{D})^2\rangle]d\mathbf{x} + \frac{1}{kT}\int_\Omega [\langle\nabla\mu\cdot(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle \\
&\quad - \bar{V}^2\langle(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle\cdot\Lambda^{-1}\cdot\langle(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle + \langle\mathcal{R}\mu\cdot D_r\mathcal{R}\mu\rangle]d\mathbf{x},
\end{aligned}
\tag{48}
$$

where

$$
\frac{d^*}{dt} = \frac{1}{kT}\nabla\cdot(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot f[\nabla\mu - \bar{V}^2\Lambda^{-1}\cdot\langle\big(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm})\big)\cdot\nabla\mu\rangle] + \frac{1}{kT}\mathcal{R}\cdot(D_r(\mathbf{m})f\mathcal{R}\mu). \tag{49}
$$

A necessary condition for (48) to be nonnegative definite is

$$
\langle\nabla\mu\cdot(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle - \bar{V}^2\langle(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\boldsymbol{\nabla}\mu\rangle\cdot\Lambda^{-1}\cdot\langle(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle \geqslant 0. \tag{50}
$$

Unfortunately, we are unable to establish the inequality for any $\max(D_\parallel, D_\perp) > 0$ and $D_\parallel, D_\perp \geqslant 0$. For a special case $D_\parallel = D_\perp$, however,

$$
(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm})) = D_\parallel\mathbf{I}, \tag{51}
$$

$$
\begin{aligned}
&\langle\nabla\mu\cdot(D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\nabla\mu\rangle - \bar{V}^2\langle(\mathbf{D}_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\cdot\mu\rangle\cdot\Lambda^{-1}\cdot\langle(\mathbf{D}_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm}))\mu\rangle \\
&\quad = D_\parallel\langle\|\nabla\mu\|^2\rangle - \bar{V}^2(D_\phi\phi+\bar{V}^2\langle 1\rangle D_\parallel)^{-1}D_\parallel^2\|\langle\nabla\mu\rangle\|^2 \\
&\quad = (D_\phi\phi+\bar{V}^2D_\parallel\langle 1\rangle)^{-1}[(D_\phi\phi+\bar{V}^2D_\parallel\langle 1\rangle)D_\parallel\langle\|\nabla\mu\|^2\rangle - \bar{V}^2D_\parallel\|\langle\nabla\mu\rangle\|^2] \\
&\quad = (D_\phi\phi+\bar{V}^2D_\parallel\langle 1\rangle)^{-1}[(D_\phi\phi)D_\parallel\langle\|\nabla\mu\|^2\rangle + \bar{V}^2D_\parallel^2(\langle\|\nabla\mu\|^2\rangle\langle 1\rangle - \bar{V}^2D_\parallel\|\langle\nabla\mu\rangle\|^2)] \geqslant (D_\phi\phi+\bar{V}^2D_\parallel\langle 1\rangle)^{-1}[(D_\phi\phi)D_\parallel\langle\|\nabla\mu\|^2\rangle] \geqslant 0,
\end{aligned}
\tag{52}
$$

where the Holder inequality [17]

$$
\|\langle\nabla\mu\rangle\|^2 \leqslant \langle\|\nabla\mu\|^2\rangle\langle 1\rangle \tag{53}
$$

is used. Thus positive entropy production is satisfied and thereby the second law of thermodynamics. In other cases, we conjecture that the positive entropy production is satisfied so long as $D_\parallel$, $D_\perp \geqslant 0$. The default option is to check the inequality (50) to ensure the positive entropy production after solving for the density function for any given values of $D_\parallel$ and $D_\perp$.

IV. APPROXIMATE THEORIES

The kinetic theory developed above has a nonlocal effective intermolecular potential μ. The elastic stress expression is therefore nonlocal. Moreover, the nonlocality also induces

an extra elastic body force that could not be written as the divergence of an elastic stress tensor, thereby leading to a nontrivial elastic body torque on the material point in the mixture. If one were to derive mesoscopic differential constitutive equations for the orientation tensor, the nonlocality would pose a significant problem. In order to overcome this difficulty, we propose a gradient expansion scheme for the density function f and the volume fraction function ϕ of the polymer, in which the free energy functional is rewritten so that, after the functions are expanded in Taylor series, the intermolecular potential is eventually given by the gradients of the density function.

We rewrite the free energy functional in the following equivalent form suitable for series expansions of the density function f and the polymer volume fraction ϕ:

$$F_{lc} = kT\int_\Omega \int_{\|\mathbf{m}\|=1} \left(f\ln f - f + \tfrac{1}{2}U(\mathbf{m},\mathbf{x},t)f(\mathbf{m},\mathbf{x},t)\right)d\mathbf{x},$$

$$U(\mathbf{m},\mathbf{x},t) = \int_{B(0,R)}\int_{S(0)}\int_{\|\mathbf{m}'\|=1} C\|\mathbf{m}\times\mathbf{m}'\| \times f(\mathbf{x}+\mathbf{x}'+\mathbf{x}'',\mathbf{m}',t)d\mathbf{x}'d\mathbf{x}''d\mathbf{m}',$$

$$F_{int} = \frac{kT\chi}{L}\int_\Omega \int_{-L/2}^{L/2}\int_{\|\mathbf{m}\|=1} \phi(\mathbf{x}+\mathbf{m}x',t)f(\mathbf{m},\mathbf{x},t)dx'd\mathbf{m}\,d\mathbf{x}. \tag{54}$$

Expanding the density function $f(\mathbf{m},\mathbf{x}+\mathbf{x}'+\mathbf{x}'',t)$ for RN-LCPs and the volume fraction of polymer $\phi(\mathbf{x}+\mathbf{m}x',t)$ in Taylor series at $\mathbf{x}$, we have

$$f(\mathbf{x}+\mathbf{x}'+\mathbf{x}'',\mathbf{m},t) = f(\mathbf{x},\mathbf{m},t) + \nabla f\cdot(\mathbf{x}'+\mathbf{x}'') + \tfrac{1}{2}\nabla\nabla f:(\mathbf{x}'+\mathbf{x}'')(\mathbf{x}'+\mathbf{x}'') + \cdots,$$

$$\phi(\mathbf{x}+\mathbf{m}x',\mathbf{m},t) = \phi(\mathbf{x},\mathbf{m},t) + \nabla\phi\cdot(\mathbf{m}x') + \tfrac{1}{2}\nabla\nabla\phi:(\mathbf{m}\mathbf{m}x'^2) + \cdots. \tag{55}$$

We also approximate the excluded volume formula using irreducible tensors [18–21],

$$C\|\mathbf{m}\times\mathbf{m}'\| \approx \alpha(1-\beta(\mathbf{m}\cdot\mathbf{m}')^2), \tag{56}$$

where we leave the specific form of α and β as free parameters. One set of values of (α,β) can be found in [19–21]. Our aim for the approximate theory is to apply it to model mesoscale structures which are much larger than the molecular scale; we will therefore truncate the series expansion at the quadratic order. Of course, more refined structure may be captured by retaining higher order terms. The approximate intermolecular potential is then obtained after the quadratically truncated series is substituted into the free energy formula,

$$U_a(\mathbf{x},\mathbf{m},t) = \frac{3C_1}{2}\left[\left(1+\frac{\mathcal{L}^2}{24}\Delta+\frac{l^2}{24}\mathbf{m}\mathbf{m}:\nabla\nabla\right)\Phi - \beta\left(\mathbf{I}+\frac{\mathcal{L}^2}{24}\Delta+\frac{l^2}{24}\mathbf{m}\mathbf{m}:\nabla\nabla\right)\langle\mathbf{m}\mathbf{m}\rangle:\mathbf{m}\mathbf{m}\right], \tag{57}$$

where $C_1=(2\alpha/3)v(B)v(S)$ and $\mathcal{L}$ and l are functions of R and L. We denote the symmetrized version by

$$\bar{U}_a(\mathbf{x},\mathbf{m},t) = \frac{3C_1}{2}\left[\left(1+\frac{\mathcal{L}^2}{24}\Delta+\frac{l^2}{48}\mathbf{m}\mathbf{m}:\nabla\nabla\right)\Phi+\frac{l^2}{48}\nabla\nabla:\mathbf{M} - \beta\left[\left(\mathbf{I}+\frac{\mathcal{L}^2}{24}\Delta+\frac{l^2}{48}\mathbf{m}\mathbf{m}:\nabla\nabla\right)\mathbf{M}:\mathbf{m}\mathbf{m} + \frac{l^2}{48}\mathbf{m}\mathbf{m}\nabla\nabla::\mathbf{M}_4\right]\right], \tag{58}$$

which yields the equal bulk free energy as U does, and

$$\mathbf{M} = \langle\mathbf{m}\mathbf{m}\rangle, \quad \mathbf{M}_4 = \langle\mathbf{m}\mathbf{m}\mathbf{m}\mathbf{m}\rangle. \tag{59}$$

The symbol $::$ and $:$ denote the tensor index contraction with respect to four indices and two, respectively. The approximate free energy is then given by

$$A^{(a)}[f] = \int_\Omega\int_{\|\mathbf{m}\|}\left[f\ln f - f + \tfrac{1}{2}\bar{U}_a f\right]d\mathbf{m}\,d\mathbf{x} + F_{poly} + F_{polyrouse} + kT\chi\int_\Omega\int_{\|\mathbf{m}\|=1}\left(1+\frac{L^2}{24}\mathbf{m}\mathbf{m}:\nabla\nabla\right)\phi f d\mathbf{m}\,d\mathbf{x} + \gamma kT\int_\Omega\left\langle\!\!\left\langle \ln\theta + \xi\sum_{i=1}^{n-1}\|\mathbf{R}_{i+1}-\mathbf{R}_i\|^2\right\rangle\!\!\right\rangle\phi d\mathbf{x}. \tag{60}$$

The effective chemical potential is calculated as

$$\mu_a = kT(\ln f + \bar{U}_a) + \chi kT\left(\phi + \frac{L^2}{24}\mathbf{m}\mathbf{m}:\nabla\nabla\phi\right) - \bar{V}\bar{\mu}_\phi,$$

$$\bar{\mu}_\phi = kT\left(\frac{1}{n}(\ln\phi+1)+2\chi_p\phi - b^2\Delta\phi\right) + \chi kT\left(\Phi+\frac{L^2}{24}\nabla\nabla:\mathbf{M}\right) + \gamma kT\left\langle\!\!\left\langle \ln\theta + \xi\sum_{i=1}^{n-1}\|\mathbf{R}_{i+1}-\mathbf{R}_i\|^2\right\rangle\!\!\right\rangle. \tag{61}$$

After a lengthy derivation, summarized in Appendix B, we arrive at the elastic stress

$$\tau_e^{(a)} = -\langle \mathbf{m} \times \mathcal{R}\mu_a \mathbf{m}\rangle + \frac{C_1 kT\mathcal{L}^2}{32}[\nabla\Phi\,\nabla\,\Phi - \Phi\,\nabla\,\nabla\Phi] + \frac{C_1 kTl^2}{64}[\nabla\Phi\,\nabla\,\cdot\mathbf{M} - \nabla\nabla\Phi\cdot\mathbf{M} + (\nabla\mathbf{M})\cdot\nabla\Phi - (\nabla\nabla\cdot\mathbf{M})\Phi] - \frac{\beta C_1 kT\mathcal{L}^2}{32}[\nabla\mathbf{M}:\nabla\mathbf{M} - (\nabla\nabla\mathbf{M}):\mathbf{M}] + \frac{\beta C_1 kTl^2}{64}[\nabla\nabla\mathbf{M}:\mathbf{M}_4 + (\nabla\nabla\cdot\mathbf{M}_4):\mathbf{M} - \nabla\mathbf{M}:(\nabla\cdot\mathbf{M}_4) - \nabla\mathbf{M}_4 \vdots \nabla\mathbf{M}] - kTb^2\,\nabla\,\phi\,\nabla\,\phi + \frac{L^2}{24}kT\chi[\nabla\phi\,\nabla\,\cdot\mathbf{M} - (\nabla\nabla\phi)\cdot\mathbf{M}] + \gamma kT\xi\phi\left\langle\left\langle\sum_{i=1}^{n-1}(\mathbf{R}_{i+1}-\mathbf{R}_i)(\mathbf{R}_{i+1}-\mathbf{R}_i)\right\rangle\right\rangle. \tag{62}$$

Since the chemical potential depends on the density function f through its gradients, the extra elastic body force is identifiable with an extra elastic stress tensor which has been incorporated into the stress expression. That is, no irreducible elastic body force is present in the approximate local theory.

With the approximate effective intermolecular potential, the Smoluchowski equation for the density function f is again given by (45) except that the effective chemical potential is given by (61). The inequality on entropy production can be established analogously provided the same condition on the mobility matrix is satisfied. The time evolution equation for ϕ is again given by (28) with the approximate chemical potential (61).

It is well known that the truncated gradient expansion is valid only for long waves [5]. We therefore anticipate an analogous limitation of the approximate theory applied to the flowing mixture system.

V. MODELS FOR FLOW-DRIVEN BULK MONODOMAINS

For a homogeneous monodomain, the theory reduces essentially to a linear combination of the Doi kinetic theory and the kinetic theory for the Rouse chains with a volume fraction weighted stress tensor.

For the Rouse model, there exists a normal mode transformation that decouples the chain $\{\mathbf{R}_i\}$ into $n-1$ independent modes $\{\mathbf{q}_i\}$ [22]. Correspondingly, the PDF θ decouples into $n-1$ independent PDFs for each mode:

$$\theta = \Pi_{i=1}^{n-1}\theta_i(\mathbf{q}_i). \tag{63}$$

The normal mode decomposition preserves

$$\sum_{i=1}^{n-1}\langle\langle(\mathbf{R}_{i+1}-\mathbf{R}_i)(\mathbf{R}_{i+1}-\mathbf{R}_i)\rangle\rangle = \sum_{i=1}^{n-1}\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle. \tag{64}$$

The Smoluchowski equation for each mode is given by

$$\frac{d\theta_i}{dt} = -\frac{\partial}{\partial\mathbf{q}_i}\cdot([\mathbf{K}-(1-a)\mathbf{D}]\cdot\mathbf{q}_i\theta_i) + \frac{\partial}{\partial\mathbf{q}_i}\cdot\mathbf{H}_i\cdot\left(\frac{\partial}{\partial\mathbf{q}_i}\mu_\theta^{(i)}\theta_i\right), \tag{65}$$

where $\mathbf{H}_i=(1/\zeta_p^{(i)})\mathbf{I}$ is the mobility matrix with the friction parameter $\zeta_p^{(i)}=\zeta_p/\sin^2(i\pi/2(n))$, ζ_p is a nominal friction parameter, and $\mu_\theta^{(i)}$ the chemical potential for mode $\mathbf{q}_i$

$$\mu_\theta^{(i)} = \gamma kT[\ln\,\theta_i + \xi\|\mathbf{q}_i\|^2]. \tag{66}$$

The extra stress tensor is given by

$$\tau = 2\eta_v\mathbf{D} + 2kT\zeta\mathbf{D}:\langle\mathbf{mmmm}\rangle - \langle\mathbf{m}\times\mathcal{R}\mu_{lc}\mathbf{m}\rangle + 2kT\phi\gamma\xi\sum_{i=1}^{n-1}\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle, \tag{67}$$

which is a volume fraction weighted extra stress from the Doi theory for NLCPs and from the Rouse model. When the volume fraction $\phi=1$, we recover completely the Rouse stress; whereas when $\phi=0$, we have the Doi stress. Taking the second moment of $\mathbf{q}_i$ with respect to θ_i, we arrive at the evolution equation for $\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle$:

$$\frac{d}{dt}\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle - \mathbf{W}\cdot\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle + \langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle\cdot\mathbf{W} - a[\mathbf{D}\cdot\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle + \langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle\cdot\mathbf{D}] = \frac{2kT\gamma}{\zeta_p^{(i)}}\mathbf{I} - \frac{4\xi kT\gamma}{\zeta_p^{(i)}}\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle. \tag{68}$$

This is the Johnson-Segalman model [22]. With this, we can completely ignore the kinetic equation for θ_i with respect to the ith mode.

As a simple demonstration, we evaluate the apparent viscosity and the normal stress differences in simple shear flows with shear rate μ: $\mathbf{v}=(\mu y,0,0)^T$. We show these using an approximate tensor-based model resulting from the closure approximation:

$$\langle\mathbf{mmmm}\rangle_{ijkl} = \Phi\left[a_0\mathbf{Q}_{ij}\mathbf{Q}_{kl} + \frac{1-a_0}{2}(\mathbf{I}_{ik}\mathbf{Q}_{jl} + \mathbf{Q}_{ik}\mathbf{I}_{jl})\right], \tag{69}$$

where a_0 is an interpolation ($|a_0|<1$) or extrapolation ($|a_0|>1$) parameter and

$$\mathbf{Q} = \frac{1}{\Phi}\langle\mathbf{mm}\rangle \tag{70}$$

is the structure tensor for RNLCPs [6]. We note that f/Φ is the probability density function for the RNLCPs provided $\Phi\neq 0$ so that

$$\mathrm{tr}(\mathbf{Q}) = 1. \tag{71}$$

The approximate intermolecular potential for the RNLCP is

$$\bar{U}_a = -\frac{3N\Phi}{2}\mathbf{mm}:\mathbf{Q}, \tag{72}$$

with dimensionless concentration N [6]. The time evolution equation for $\mathbf{Q}$ in the kinetic theory is given by

$$\frac{d}{dt}\mathbf{Q}-\mathbf{W}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{W}-[\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D}]=-\frac{2\mathbf{D}}{\Phi}:\langle\mathbf{mmmm}\rangle-6Dr[\mathbf{Q}-\mathbf{I}/3-N(1-\phi)\mathbf{Q}\cdot\mathbf{Q}+N(1-\phi)/\Phi\mathbf{Q}:\langle\mathbf{mmmm}\rangle], \tag{73}$$

which is obtained by taking the second moment of $\mathbf{m}$ with respect to the NDF f. After applying closure (69), the equation is approximated by

$$\frac{d}{dt}\mathbf{Q}-\mathbf{W}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{W}-a_0[\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D}]=-2a_0\mathbf{D}:\mathbf{QQ}-6Dr[\mathbf{Q}-\mathbf{I}/3-a_1N(1-\phi)\mathbf{Q}\cdot\mathbf{Q}+a_1N(1-\phi)\mathbf{Q}:\mathbf{QQ}], \tag{74}$$

where $a_1\in[-1,1]$ is an interpolating parameter. With the help of the orientation tensor equation, the extra stress tensor becomes

$$\begin{aligned}\tau&=2\eta_v\mathbf{D}+2kT\zeta\mathbf{D}:\langle\mathbf{mmmm}\rangle+2kT\phi\gamma\xi\sum_{i=1}^{n-1}\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle+3kT\Phi[\mathbf{Q}-\mathbf{I}/3-N(1-\phi)\mathbf{Q}\cdot\mathbf{Q}+N(1-\phi)\mathbf{Q}:\langle\mathbf{mmmm}\rangle/\Phi]\\&=-\frac{3kT\Phi}{6Dr}\left[\frac{d}{dt}\mathbf{Q}-\mathbf{W}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{W}-[\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D}]\right]+2\eta_v\mathbf{D}+2kT\left(\zeta-\frac{a_0}{2Dr}\right)\mathbf{D}:\langle\mathbf{mmmm}\rangle+2kT\phi\gamma\xi\sum_{i=1}^{n-1}\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle\\&=-\frac{3kT\Phi}{6Dr}\left[\frac{d}{dt}\mathbf{Q}-\mathbf{W}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{W}-a_0[\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D}]\right]+2\eta_v\mathbf{D}+2\tilde{a}_0kT\left(\zeta-\frac{1}{2Dr}\right)\Phi\mathbf{D}:\mathbf{QQ}\\&\quad+(1-\tilde{a}_0)kT\zeta\Phi(\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D})+2kT\phi\gamma\xi\sum_{i=1}^{n-1}\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle.\end{aligned} \tag{75}$$

We introduce a polymeric stress tensor for flexible polymers

$$\tau_p^{(i)}=\gamma kT\xi\left(2\langle\langle\mathbf{q}_i\mathbf{q}_i\rangle\rangle-\frac{1}{\xi}\mathbf{I}\right). \tag{76}$$

The time evolution equation for $\tau_p^{(i)}$ follows from (68)

$$\begin{aligned}&\frac{d}{dt}\tau_p^{(i)}-\mathbf{W}\cdot\tau_p^{(i)}+\tau_p^{(i)}\cdot\mathbf{W}-a[\mathbf{D}\cdot\tau_p^{(i)}+\tau_p^{(i)}\cdot\mathbf{D}]+\frac{\tau_p^{(i)}}{\lambda_i}\\&\quad=2\frac{\eta_p^{(i)}}{\lambda_i}\mathbf{D},\end{aligned} \tag{77}$$

where $\lambda^{(i)}=\zeta_p^{(i)}/4kT\xi\gamma$ is the polymer relaxation time and $\eta_p^{(i)}=a\zeta_p^{(i)}/4\xi$ is the polymeric viscosity. The extra stress further reduces to

$$\begin{aligned}\tau=&-\frac{3kT\Phi}{6Dr}\left[\frac{d}{dt}\mathbf{Q}-\mathbf{W}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{W}-a_0[\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D}]\right]\\&+2\eta_v\mathbf{D}+2a_0kT\left(\zeta-\frac{1}{2Dr}\right)\Phi\mathbf{D}:\mathbf{QQ}\\&+(1-a_0)kT\zeta\Phi(\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D})\\&+\phi\sum_{i=1}^{n-1}\tau_p^{(i)}+\text{const}\times\mathbf{I}.\end{aligned} \tag{78}$$

Using the RNLCP relaxation time as the characteristic time $t_0=1/6Dr$ and the gap width (h) of the shearing device as the characteristic length scale, we arrive at a dimensionless group

$$\mathrm{Pe}=\frac{1}{\mu t_0},\quad \mathrm{De}_p^{(i)}=\frac{\lambda^{(i)}}{t_0},\quad \mathrm{Re}=\frac{\rho h}{\eta_v t_0},\quad \mathrm{Re}_p^{(i)}=\frac{f_0}{\eta_p^{(i)}h}, \tag{79}$$

$\mathrm{Re}_{lcp}=6Dr/kT$, $\mathrm{Re}_{lcp}^{v}=1/\zeta kT$,where Pe is the Peclet number, $\mathrm{De}_p^{(i)}$ is the Deborah numbers for the ith mode of the flexible polymer, where $i=1,\ldots,N,\mathrm{Re},\mathrm{Re}_p^{(i)},\mathrm{Re}_{lcp},\mathrm{Re}_{lcp}^{v}$ are the Reynolds numbers parametrizing the viscosity coefficients in the model for the mixture, and $f_0=\rho h^2/t_0^2$ is a characteristic stress that is chosen as the inertia stress here. The extra stress in dimensionless form is given by

$$\begin{aligned}\tau=&\left[-\frac{3}{\mathrm{Re}_{lcp}}\left[\frac{d}{dt}\mathbf{Q}-\mathbf{W}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{W}-a_0[\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D}]\right]\right.\\&+\frac{2}{\mathrm{Re}}\mathbf{D}+2a_0\left(\frac{1}{\mathrm{Re}_{lcp}^{v}}-\frac{3}{\mathrm{Re}_{lcp}}\right)\mathbf{D}:\mathbf{QQ}+(1-a_0)\\&\left.\times\left(\frac{1}{\mathrm{Re}_{lcp}^{v}}\right)(\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D})\right](1-\phi)+\phi\sum_{i=1}^{n-1}\tau_p^{(i)}.\end{aligned} \tag{80}$$

The dimensionless orientation tensor equation and the equation for $\tau_p^{(i)}$ are given respectively by

$$\begin{aligned}&\frac{d}{dt}\mathbf{Q}-\mathbf{W}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{W}-a_0[\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D}]\\&\quad=-2a_0\mathbf{D}:\mathbf{QQ}-\frac{1}{\mathrm{De}}[\mathbf{Q}-\mathbf{I}/3-a_1N(1-\phi)\mathbf{Q}\cdot\mathbf{Q}\\&\qquad+a_1N(1-\phi)\mathbf{Q}:\mathbf{QQ}],\end{aligned}$$

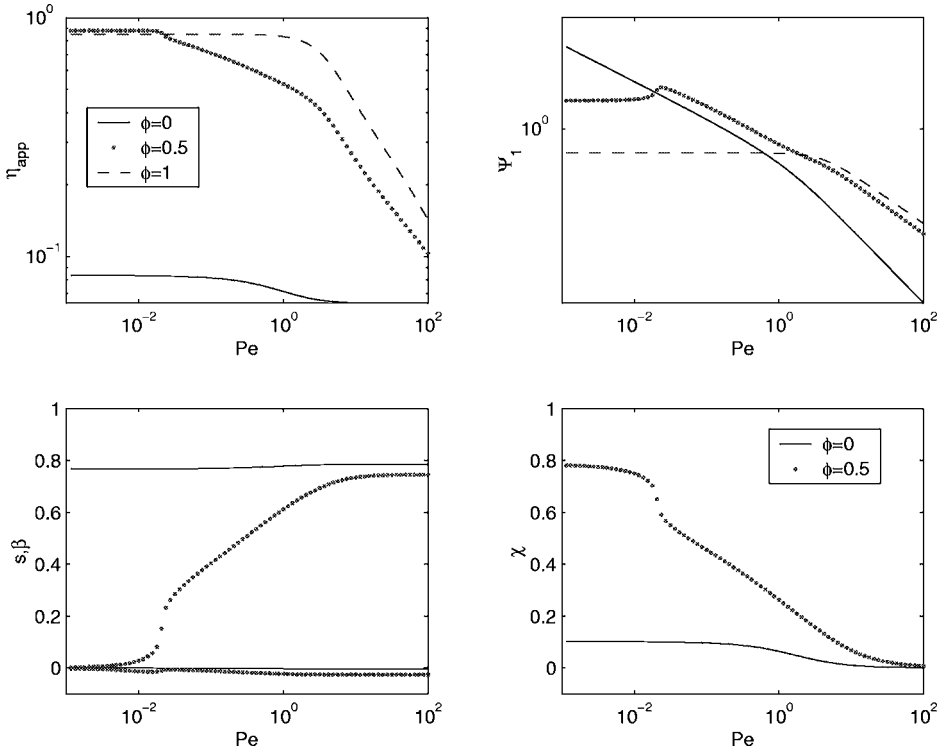

FIG. 1. The apparent shear viscosity, primary normal stress coefficient, order parameters, and the Leslie angle as functions of the Peclet number for Johnson-Segalman fluids ($\phi=1$, dashed curves), half-half RNLCP-polymer mixture ($\phi=1/2$, dotted curves), and RNLCPs ($\phi=0$, solid curves). Re=20, $\mathrm{Re}_{lcp}=1$, $\mathrm{Re}^{v}_{lcp}=5$, $\mathrm{Re}^{0}_{p}=100$, $\mathrm{De}^{0}_{p}=0.01$, $N=6$, $a=\bar{a}_0=a_1=0.85$, $a_0=1$, where $\mathrm{Re}^{(i)}_{p}=1/\mathrm{Re}^{0}_{p}\sin^2(i\pi/2n)$, $\mathrm{De}^{(i)}_{p}=\mathrm{De}^{0}_{p}/\sin^2(i\pi/2n)$. 10 Rouse modes are used, i.e., $n=11$. Shear thinning for all fluids. "Isotropic-to-nematic" phase transition is present in the mixture, which shows up in the apparent viscosity ($\eta_{\mathrm{app}}=\tau_{xy}/\mathrm{Pe}$) and the primary normal stress coefficient $\Psi_1=N_1/\mathrm{Pe}^2$.

$$\frac{d}{dt}\tau_p^{(i)} - \mathbf{W}\cdot\tau_p^{(i)} + \tau_p^{(i)}\cdot\mathbf{W} - a[\mathbf{D}\cdot\tau_p^{(i)} + \tau_p^{(i)}\cdot\mathbf{D}] + \frac{\tau_p^{(i)}}{\mathrm{De}_p} = \frac{2}{\mathrm{De}_p^{(i)}\,\mathrm{Re}_p^{(i)}}\mathbf{D}. \tag{81}$$

The steady shear stress and the normal stress differences for the flexible polymer part can be easily calculated for the ith mode:

$$\tau_{pxy}^{(i)} = \frac{\mu}{\mathrm{Re}_p^{(i)}(1+(1-a^2)\mu^2(\mathrm{De}_p^{(i)})^2)},$$

$$N_{p1}^{(i)} = \frac{2\mu^2\mathrm{De}_p^{(i)}}{\mathrm{Re}_p^{(i)}(1+(1-a^2)\mu^2(\mathrm{De}_p^{(i)})^2)},$$

$$N_{p2}^{(i)} = -\frac{(1-a)\mu^2\mathrm{De}_p^{(i)}}{\mathrm{Re}_p^{(i)}(1+(1-a^2)\mu^2(\mathrm{De}_p^{(i)})^2)}. \tag{82}$$

The corresponding ones from the RNLCP contribution are tedious and thus omitted.

Figure 1 plots the steady state apparent shear viscosity defined as the ratio of the shear stress to the shear rate, the primary normal stress coefficient defined as the ratio of the first normal stress difference to the square of the shear rate, the order parameters (s,β) and the major director angle ψ with respect to three volume fractions $\phi=0,0.5,1$ sampling the limit of pure Johnson-Segalman (JS) fluids, mixture of half RNLCP and half flexible polymer, and the limit of Doi RNLCPs, respectively. Here the orientation tensor is written into its spectral decomposition

$$\mathbf{Q} = \frac{\mathbf{I}}{3} + s\left(\mathbf{nn} - \frac{\mathbf{I}}{3}\right) + \beta\left(\mathbf{n}^{\perp}\mathbf{n}^{\perp} - \frac{\mathbf{I}}{3}\right),$$

$$\mathbf{n} = (\cos\psi, \sin\psi, 0), \quad \mathbf{n}^{\perp} = (-\sin\psi, \cos\psi, 0). \tag{83}$$

The mixture exhibits shear thinning behavior since both the JS fluid and RNLCP do. In the semidilute limit of the mixture, a phase transition takes place leading to a noticeable change in the apparent shear viscosity as well as the primary normal stress coefficient. Before the phase transition, the apparent shear viscosity in the mixture is larger than the one in the pure JS fluid. After the phase transition however, a noticeable reduction in the viscosity is shown. The primary normal stress coefficient of the mixture also exhibits a crossover with that of the pure RNLCP at the phase transition Peclet number. Figure 2 depicts the storage G' and the loss G'' module calculated from the model at the three distinct values of volume fraction. We defer a more detailed study on the rhological predictions of the model to a sequel.

VI. MODEL EXTENSIONS

From the derivation of the theory, we notice that the conformational dynamics of the flexible polymer essentially decouples from the dynamics of their center of mass as well as the dynamics of the RNLCPs due to the separable assumption. This indicates that we can literally replace this part of the theory by any kinetic theory of polymers for bulk monodomains so long as they are spatially homogeneous. For example, the Rouse dynamics can be replaced in the theory by that of FENE, FENE-p, Giesekus model, etc. Another consequence of the derivation is that the resultant elastic stress contains a volume fraction averaged polymeric stress from the homogeneous kinetic theory of polymers. The ef-

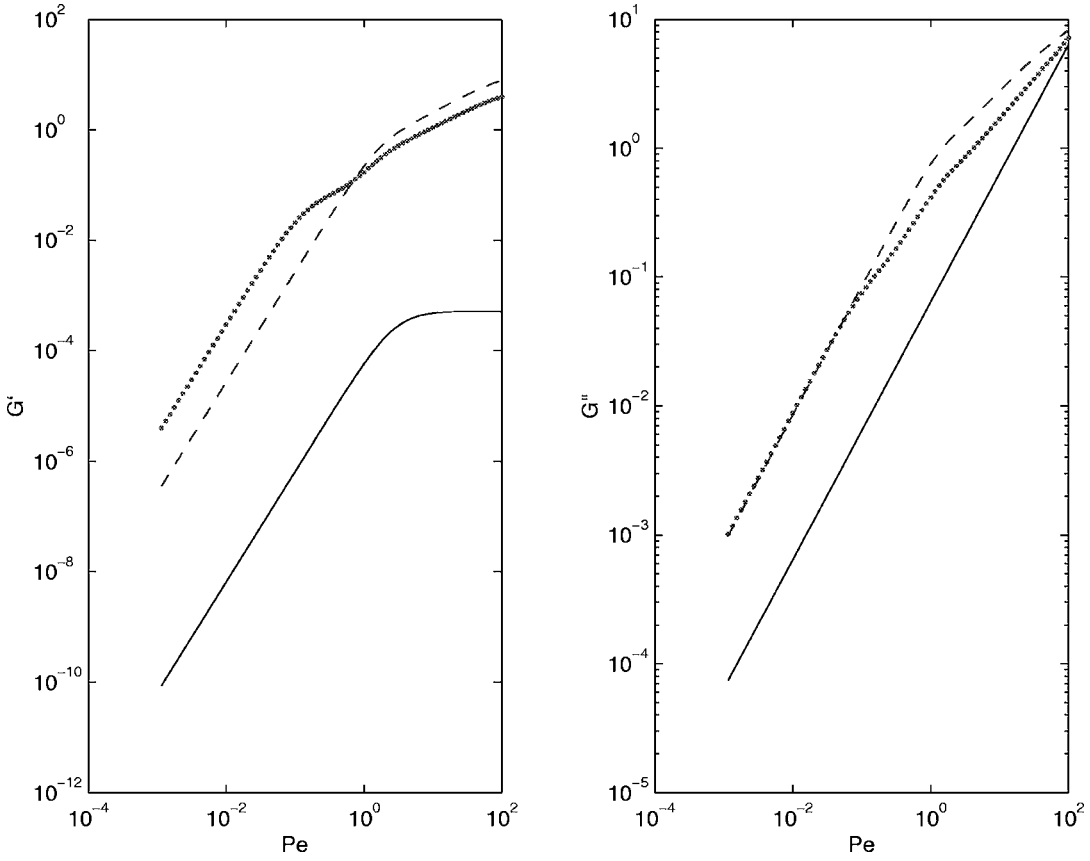

FIG. 2. The storage and loss module (G', G'') as functions of the Peclet number for Johnson-Segalman fluids ($\phi=1$, dashed curves), half-half RNLCP-polymer mixture ($\phi=1/2$, dotted curves), and RNLCPs ($\phi=0$, solid curves). The parameter values are identical to those in Fig. 1.

fective strength of the intermolecular potential is parametrized by the product of the dimensionless concentration and the volume fraction of the RNLCP: $N(1-\phi)$. As the volume fraction of RNLCPs decreases, the intermolecular interaction weakens leading to the phase transition behavior at small volume fractions.

VII. CONCLUSION

A hydrodynamic theory for incompressible polymer-LCP mixtures has been developed generalizing the kinetic theory for phase separation kinetics derived by Muratov and E [5]. We modified the translational flux for the density function f in [5] so that the incompressibility constraint is upheld exactly. We added the detailed viscoelastic dynamics of flexible polymers modeling the flexible polymer as a Rouse chain. We then show that the elasticity due to the nonlocal (long-range) molecular interaction contributes not only to the stress tensor, but also to an extra body force. The extra elastic body force is intimately related to the nonlocality of the intermolecular potential, in that it would be a divergence of a second order tensor were the chemical potential local and thereby would be absorbed into the elastic stress tensor. With our modified translational fluxes, we establish positive entropy production and thereby the second law of thermodynamics for the theory, provided a necessary condition for the mobility matrix to satisfy. This theory gives the explicit relation between the stress of the RNLCP and that of the flexible polymer by a volume fraction weighted extra stress formula. It provides the crucial coupling between kinetic theory and momentum transport, and lays the foundation for study of the hydrodynamics of the flowing mixture.

We then derive an approximate, differential theory by approximating the density function of the RNLCP and the volume fraction of the flexible polymer by their truncated Taylor series. Consequently, the free energy in the approximate theory depends on the density function and the volume fraction as well as their gradients explicitly. Through the virtual work principle, we derive the expression for the elastic stress tensor, which includes extra terms whose divergence would be part of the extra elastic body force were the free energy nonlocal.

This theory and its approximations provide a platform for studying flows of LCP-polymer mixtures, of which rodlike nematic polymer nano-composites are primary examples. The nonlocal theory is suitable for a stochastic simulation with equivalent Langevin equations (stochastic odes) for the spatial variables $\mathbf{x}$ and the configurational variable $\mathbf{m}$ [23]. On the other hand, the approximate theory is better suited for a direct numerical simulation of the Smoluchowski equation or further approximations based on moments of the density function f. Further evaluation of the theory on benchmark problems is currently underway.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF THE ELASTIC STRESS TENSOR AND THE EXTRA ELASTIC BODY FORCE FOR THE THEORY OF A NONLOCAL INTERMOLECULAR POTENTIAL

Consider an infinitesimal displacement given by $\delta\mathbf{u}=\mathbf{v}\delta t$ and the corresponding deformation $\delta\epsilon=K\delta t$. The variation of the density function f in response to the infinitesimal deformation is given by the variation of the density function f along the path of the material point [6]

$$\delta f = \frac{df}{dt}\delta t = -\mathcal{R}\cdot(\mathbf{m}\times\dot{\mathbf{m}}f)\delta t. \tag{A1}$$

We then calculate the variation of the free energy with respect to δf:

$$\delta F_{lc} = kT\int_\Omega\int_{\|\mathbf{m}\|=1}\left[\left(\ln f+\tfrac{1}{2}U\right)\delta f+\tfrac{1}{2}f\delta U\right]d\mathbf{m}\,d\mathbf{x}. \tag{A2}$$

The variation of the intermolecular potential with respect to δf defined by (A1) is obtained as follows:

$$\begin{aligned}
\delta U &= \frac{d}{dt}\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t\\
&= \int_{\Omega^2}\int_{\|\mathbf{m}'\|=1}\mathbf{v}(\mathbf{x},t)\cdot\nabla B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t\\
&\quad+\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')\frac{\partial}{\partial t}f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t\\
&= \int_{\Omega^2}\int_{\|\mathbf{m}'\|=1}\mathbf{v}(\mathbf{x},t)\cdot\nabla B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t\\
&\quad+\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')\frac{d}{dt}f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t\\
&\quad-\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')\mathbf{v}(\mathbf{x}'',t)\cdot\nabla_{x''}f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t.
\end{aligned} \tag{A3}$$

Using integration by parts,

$$\begin{aligned}
&\int_\Omega\int_{\|\mathbf{m}\|=1}\delta U(\mathbf{m},\mathbf{x},t)d\mathbf{m}\,d\mathbf{x}\\
&= \int_\Omega\int_{\|\mathbf{m}\|=1} f(\mathbf{m},\mathbf{x},t)\left[\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1}\mathbf{v}(\mathbf{x},t)\cdot\nabla B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t\right.\\
&\quad+\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')\frac{d}{dt}f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\delta t\\
&\quad\left.-\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1} B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')\mathbf{v}(\mathbf{x}'',t)\cdot\nabla_{x''}f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'\right]d\mathbf{x}\,d\mathbf{m}\,\delta t\\
&= \int_\Omega\int_{\|\mathbf{m}\|=1} f(\mathbf{m},\mathbf{x},t)\left[\int_{\Omega^2}\int_{\|\mathbf{m}'\|=1}\mathbf{v}(\mathbf{x},t)\cdot\nabla B(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}')H(\mathbf{m}',\mathbf{x}'-\mathbf{x}'')f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''\right]d\mathbf{x}'d\mathbf{m}'\delta t\\
&\quad+\int_\Omega\int_{\|\mathbf{m}\|=1} U_2\delta f d\mathbf{m}\,d\mathbf{x}+\int_{\Omega^3}\int_{\|\mathbf{m}\|=1}\int_{\|\mathbf{m}'\|=1} f(\mathbf{m}',\mathbf{x}'',t)\mathbf{v}(\mathbf{x},t)\cdot\nabla_x B(\mathbf{m}',\mathbf{m},\mathbf{x}''-\mathbf{x}')\\
&\quad\times H(\mathbf{m},\mathbf{x}'-\mathbf{x})f(\mathbf{m},\mathbf{x},t)d\mathbf{x}''d\mathbf{x}'d\mathbf{m}'d\mathbf{x}\,d\mathbf{m}\,\delta t\\
&= \int_\Omega\int_{\|\mathbf{m}\|=1}[U_2\delta f+\mathbf{v}\cdot\nabla(U+U_2)f(\mathbf{m},\mathbf{x},t)\delta t]d\mathbf{m}\,d\mathbf{x}.
\end{aligned} \tag{A4}$$

Then, using the definition of U_2 and integration by part, the variation of the free energy can be rearranged to the following form:

$$\delta F_{lc} = kT\left[\int_\Omega \int_{\|\mathbf{m}\|=1} \left(\ln f + \frac{1}{2}(U+U_2)\right)\delta f + \frac{1}{2}\mathbf{v}(\mathbf{x},t)\cdot\nabla(U+U_2) f \delta t\right] d\mathbf{m}\, d\mathbf{x}, \tag{A5}$$

where

$$\mu_1 = kT\left(\ln f + \frac{1}{2}(U+U_2)\right). \tag{A6}$$

Notice that

$$\begin{aligned}
&\int_\Omega \int_{\|\mathbf{m}\|=1} \mu_1 \delta f d\mathbf{m}\, d\mathbf{x} \\
&= \int_\Omega \int_{\|\mathbf{m}\|=1} \mu_1 \frac{\delta f}{dt}\delta t d\mathbf{m}\, d\mathbf{x} \\
&= -\int_\Omega \int_{\|\mathbf{m}\|=1} \mu_1 \mathcal{R}\cdot(\mathbf{m}\times\mathbf{K}\cdot\mathbf{m} f)\delta t d\mathbf{m}\, d\mathbf{x} \\
&= \int_\Omega \int_{\|\mathbf{m}\|=1} \mathcal{R}\mu_1\cdot(\mathbf{m}\times\mathbf{K}\cdot\mathbf{m} f)\delta t d\mathbf{m}\, d\mathbf{x} \\
&= -\delta t kT\int_\Omega \mathbf{K}:\langle \mathbf{m}\times\mathcal{R}\mu_1\mathbf{m}\rangle.
\end{aligned} \tag{A7}$$

So

$$\delta F_{lc} = -\delta t kT\int_\Omega \mathbf{K}:\langle \mathbf{m}\times\mathcal{R}\mu_1\mathbf{m}\rangle d\mathbf{x} + \delta t\frac{kT}{2}\int_\Omega \mathbf{v}\cdot\langle\nabla(U+U_2)\rangle d\mathbf{x}. \tag{A8}$$

The stress contributed by this part of free energy is identified as

$$\tau^e_{lcp} = -kT\langle \mathbf{m}\times\mathcal{R}\mu_1\mathbf{m}\rangle, \tag{A9}$$

and the extra elastic body force associated to F_{lcp} is given by

$$\mathbf{F}^e_{lcp} = -kT\langle\nabla U_e\rangle, \tag{A10}$$

where

$$U_e = \frac{1}{2}(U+U_2) \tag{A11}$$

is the effective intermolecular potential. Next, we examine the contribution to the elastic stress from the free energy related to the flexible polymer by calculating the variation of $\mathbf{F}_{poly}$ with respect to $\delta\phi$:

$$\delta F_{poly} = kT\int_\Omega \left[b^2\nabla\phi\delta\nabla\phi + \left(\frac{1}{N}\ln\phi + \frac{1}{N} + 2\chi_p\phi\right)\delta\phi\right] d\mathbf{x}. \tag{A12}$$

From the incompressibility constraint, we have

$$\delta\phi + \bar{V}\int_{\|\mathbf{m}\|=1}\delta f = 0. \tag{A13}$$

From

$$\int_{\|\mathbf{m}\|=1}\delta f = \int_{\|\mathbf{m}\|=1}\mathcal{R}\cdot(\mathbf{m}\times\dot{\mathbf{m}} f)d\mathbf{m} = 0, \tag{A14}$$

it follows that

$$\delta\phi = 0. \tag{A15}$$

From (A1) and the incompressibility constraint, we notice that δ and ∇ does not commute, i.e., $\delta\nabla\phi \neq \nabla\delta\phi$. In fact,

$$\delta\nabla\phi = \delta\nabla\phi - \nabla\delta\phi = -K_{\beta,\alpha}\nabla_\beta\phi. \tag{A16}$$

Combining all above together, we have

$$\delta F_{poly} = -kT\int_\Omega b^2 K_{\alpha,\beta}\nabla_\alpha\phi\nabla_\beta\phi d\mathbf{x}\,\delta t. \tag{A17}$$

The corresponding stress contribution is given by

$$\tau^e_{poly} = -b^2 kT\nabla\phi\nabla\phi. \tag{A18}$$

Analogously, we have

$$\delta F_{polyrouse} = \int_\Omega \phi\xi K_{\alpha,\beta}\left\langle\left\langle\frac{\partial}{\partial\mathbf{R}_i}\mu_\theta\mathbf{R}_i\right\rangle\right\rangle d\mathbf{x}\,\delta t. \tag{A19}$$

This leads to

$$\tau^e_{polyrouse} = \xi\phi\left\langle\left\langle\frac{\partial}{\partial\mathbf{R}_i}\mu_\theta\mathbf{R}_i\right\rangle\right\rangle. \tag{A20}$$

Finally, we calculate the variation of the free energy responsible for the polymer-LCP interaction to obtain the stress as well as the extra elastic body force due to this effect:

$$\begin{aligned}\delta F_{int} &= kT\chi\int_{\Omega^2}\int_{\|\mathbf{m}\|=1}\Big[\phi(\mathbf{x}',t)H(\mathbf{m},\mathbf{x}-\mathbf{x}')\delta f(\mathbf{m},\mathbf{x},t)+\mathbf{v}(\mathbf{x},t)\cdot\nabla H(\mathbf{m},\mathbf{x}-\mathbf{x}')\phi(\mathbf{x}',t)f(\mathbf{m},\mathbf{x},t)\delta t\\ &\quad+\left(\frac{d}{dt}\phi(\mathbf{x}',t)-\mathbf{v}(\mathbf{x}',t)\cdot\nabla_{x'}\phi(\mathbf{x}',t)\right)H(\mathbf{m},\mathbf{x}-\mathbf{x}')f(\mathbf{m},\mathbf{x},t)\delta t\Big]d\mathbf{x}'d\mathbf{m}\,d\mathbf{x}\\ &=-kT\chi\int_{\Omega}\delta t\mathbf{K}:\left\langle\int_{\Omega}\phi(\mathbf{x}',t)\mathbf{m}\times\mathcal{R}(H(\mathbf{m},\mathbf{x}-\mathbf{x}'))d\mathbf{x}'\mathbf{m}\right\rangle d\mathbf{x}+kT\chi\int_{\Omega^2}\delta t\mathbf{v}(\mathbf{x},t)\cdot\Big[\langle\phi(\mathbf{x}',t)\,\nabla H(\mathbf{m},\mathbf{x}-\mathbf{x}')\rangle d\mathbf{x}'\\ &\quad-\int_{\|\mathbf{m}\|=1}\nabla\phi(\mathbf{x},t)H(\mathbf{m},\mathbf{x}'-\mathbf{x})f(\mathbf{m},\mathbf{x}',t)d\mathbf{m}\Big]d\mathbf{x}'d\mathbf{x}'\\ &=-kT\chi\int_{\Omega}\delta t\mathbf{K}:\left\langle\int_{\Omega}\phi(\mathbf{x}',t)\mathbf{m}\times\mathcal{R}(H(\mathbf{m},\mathbf{x}-\mathbf{x}'))d\mathbf{x}'\mathbf{m}\right\rangle+kT\chi\int_{\Omega^2}\delta t\mathbf{v}(\mathbf{x},t)\cdot[\langle\phi(\mathbf{x}',t)\,\nabla H(\mathbf{m},\mathbf{x}-\mathbf{x}')\rangle\\ &\quad+\phi(\mathbf{x},t)\langle\nabla H(\mathbf{m},\mathbf{x}'-\mathbf{x})\rangle]d\mathbf{x}'d\mathbf{x},\end{aligned}\tag{A21}$$

where integration by parts is used and

$$\langle\nabla H(\mathbf{m},\mathbf{x}-\mathbf{x}')\rangle=\int_{\|\mathbf{m}\|=1}H(\mathbf{m},\mathbf{x}-\mathbf{x}')f(\mathbf{m},\mathbf{x},t)d\mathbf{m}.\tag{A22}$$

The contribution of the free energy to the stress tensor is given by

$$\tau^{e}_{int}=-kT\chi\left\langle\int_{\Omega}\phi(\mathbf{x}',t)\mathbf{m}\times\mathcal{R}H(\mathbf{m},\mathbf{x}-\mathbf{x}')d\mathbf{x}'\mathbf{m}\right\rangle.\tag{A23}$$

The extra elastic body force is identified as

$$\begin{aligned}\mathbf{F}^{e}_{int}&=-kT\chi\int_{\Omega}[\phi(\mathbf{x}',t)\langle\nabla H(\mathbf{m},\mathbf{x}-\mathbf{x}')\rangle\\ &\quad+\phi(\mathbf{x},t)\langle\nabla H(\mathbf{m},\mathbf{x}'-\mathbf{x})\rangle]d\mathbf{x}'.\end{aligned}\tag{A24}$$

Summarizing the above calculations, we obtain the elastic stress for the mixture system

$$\begin{aligned}\tau&=\tau^{e}_{lcp}+\tau^{e}_{poly}+\tau^{e}_{int}+\tau^{e}_{polyrouse}\\ &=-\langle\mathbf{m}\times\mathcal{R}\mu_{lc}\mathbf{m}\rangle-b^2kT\nabla\phi\nabla\phi+\phi\left\langle\left\langle\frac{\partial}{\partial\mathbf{R}_i}\mu_{\theta}\mathbf{R}_i\right\rangle\right\rangle\end{aligned}\tag{A25}$$

and the extra elastic body force

$$\begin{aligned}\mathbf{F}^{e}&=\mathbf{F}^{e}_{lcp}+\mathbf{F}^{e}_{int}\\ &=-kT\Big[\langle\nabla U_e\rangle+\chi\int_{\Omega}[\phi(\mathbf{x}',t)\langle\nabla H(\mathbf{m},\mathbf{x}-\mathbf{x}')\rangle\\ &\quad+\phi(\mathbf{x},t)\langle\nabla H(\mathbf{m},\mathbf{x}'-\mathbf{x})\rangle]d\mathbf{x}\Big].\end{aligned}\tag{A26}$$

APPENDIX B: DERIVATION OF THE ELASTIC STRESS TENSOR IN THE APPROXIMATE THEORY

We derive the elastic stress for the approximate theory. We follow the same approach outlined in Appendix A and begin with the approximate free energy:

$$A^{(a)}[f]=F^{(a)}_{lc}+F_{poly}+F_{polyrouse}+F^{(a)}_{int},\tag{B1}$$

where

$$F^{(a)}_{lc}=kT\int_{\Omega}\int_{\|\mathbf{m}\|}\left[f\ln f+\tfrac{1}{2}\bar{U}f\right]d\mathbf{m}\,d\mathbf{x},\tag{B2}$$

$$\begin{aligned}\bar{U}_a&=\frac{3C_1}{2}\Big[\left(1+\frac{\mathcal{L}^2}{24}\Delta+\frac{l^2}{48}\mathbf{mm}:\nabla\nabla\right)\Phi+\frac{l^2}{48}\nabla\nabla:\mathbf{M}\\ &\quad-\beta\Big[\left(\mathbf{I}+\frac{\mathcal{L}^2}{24}\Delta+\frac{l^2}{48}\mathbf{mm}:\nabla\nabla\right)\mathbf{M}:\mathbf{mm}\\ &\quad+\frac{l^2}{48}\mathbf{mm}\nabla\nabla::\mathbf{M}_4\Big]\Big],\end{aligned}\tag{B3}$$

and

$$F^{(a)}_{int}=kt\chi\int_{\Omega}\int_{\|\mathbf{m}\|}\left(1+\frac{L^2}{24}\mathbf{mm}:\nabla\nabla\right)\phi f d\mathbf{m}\,d\mathbf{x}.\tag{B4}$$

We calculate the variation of the free energy F_{lc} with respect to the variation of the density function f:

$$\delta F_{lc}^{(a)} = \frac{d}{dt}F_{lc}^{(a)}\delta t = kT\int_\Omega\int_{\|\mathbf{m}\|=1}\left[(\ln f+\bar{U}_a)\frac{df}{dt}\delta t + \frac{1}{2}\left(\frac{d\bar{U}_a}{dt}f-\bar{U}_a\frac{df}{dt}\right)\delta t\right]d\mathbf{m}\,d\mathbf{x} = I+II, \quad \text{(B5)}$$

where

$$I = kT\int_\Omega\int_{\|\mathbf{m}\|=1}(\ln f+\bar{U}_a)\frac{df}{dt}\delta t d\mathbf{m}\,d\mathbf{x} = -\int_\Omega \mathbf{K}:\langle \mathbf{m}\times\mathcal{R}\mu_a^{(1)}\mathbf{m}\rangle d\mathbf{x}, \quad \text{(B6)}$$

where

$$\mu_a^{(1)} = kT(\ln f+\bar{U}_a), \quad \text{(B7)}$$

$$II = \frac{kT}{2}\int_\Omega\left(\frac{d\bar{U}_a}{dt}f-\bar{U}_a\frac{df}{dt}\right)d\mathbf{m}\,d\mathbf{x}\,\delta t = \frac{3C_1kT}{4}\int_\Omega\int_{\|\mathbf{m}\|=1}\left\{\frac{\mathcal{L}^2}{24}\left[\Phi\left(\frac{d}{dt}\Delta-\Delta\frac{d}{dt}\right)\Phi-\beta\left(\mathbf{M}:\left(\frac{d}{dt}\Delta-\Delta\frac{d}{dt}\right)\mathbf{M}\right)\right]\right.$$
$$+\frac{l^2}{48}\left[\left(\mathbf{M}:\left(\frac{d}{dt}\nabla\nabla-\nabla\nabla\frac{d}{dt}\right)\Phi+\left(\frac{d}{dt}\nabla\nabla-\nabla\nabla\frac{d}{dt}\right):\mathbf{M}\Phi\right)-\beta\left(\mathbf{M}_4::\left(\frac{d}{dt}\nabla\nabla-\nabla\nabla\frac{d}{dt}\right)\mathbf{M}+\mathbf{M}\left(\frac{d}{dt}\nabla\nabla-\nabla\nabla\frac{d}{dt}\right)::\mathbf{M}_4\right)\right]$$
$$+\frac{\mathcal{L}^2}{24}\left[\Phi\Delta\frac{d}{dt}\Phi-\Delta\Phi\frac{d\Phi}{dt}-\beta\left(\mathbf{M}:\Delta\frac{d\mathbf{M}}{dt}-\Delta\mathbf{M}:\frac{d}{dt}\mathbf{M}\right)\right]+\frac{l^2}{48}\left[\mathbf{M}:\nabla\nabla\frac{d}{dt}\Phi+\nabla\nabla:\frac{d}{dt}\mathbf{M}\Phi-\frac{d}{dt}\mathbf{M}:\nabla\nabla\Phi-\nabla\nabla:\mathbf{M}\frac{d}{dt}\Phi\right.$$
$$\left.\left.-\beta\left(\mathbf{M}_4::\nabla\nabla\frac{d}{dt}\mathbf{M}+\mathbf{M}\nabla\nabla::\frac{d}{dt}\mathbf{M}_4-\frac{d}{dt}\mathbf{M}_4::\nabla\nabla\mathbf{M}-\frac{d}{dt}\mathbf{M}\nabla\nabla::\mathbf{M}_4\right)\right]\right\}. \quad \text{(B8)}$$

We note that

$$\frac{d}{dt}\nabla_i\nabla_j-\nabla_i\nabla_j\frac{d}{dt} = -\nabla_i(\mathbf{K}_{ji}\nabla_j)-\mathbf{K}_{ji}\nabla_i\nabla_j,$$

$$\frac{d}{dt}\nabla_i\nabla_j-\nabla_i\nabla_j\frac{d}{dt} = -\nabla_i(\mathbf{K}_{lj}\nabla_l)-\mathbf{K}_{li}\nabla_j\nabla_l. \quad \text{(B9)}$$

Using the identities, dropping the surface terms in II, and applying integration by parts, we have

$$II = \frac{3C_1kT}{4}\int_\Omega \mathbf{K}_{ij}\left\{\frac{\mathcal{L}^2}{24}\nabla_j\Phi\nabla_i\Phi-\Phi\nabla_i\nabla_j\Phi-\beta(\nabla_i\mathbf{M}_{kl}\nabla_j\mathbf{M}_{kl}\right.$$
$$-\mathbf{M}_{kl}\nabla_i\nabla_j\mathbf{M}_{kl})+\frac{l^2}{48}[\nabla_k\mathbf{M}_{kj}\nabla_i\Phi-\nabla_k\nabla_i\Phi\mathbf{M}_{jk}$$
$$+\nabla_k\Phi\nabla_i\mathbf{M}_{kj}-\nabla_l\nabla_i\mathbf{M}_{jl}\Phi-\beta(\nabla_k\mathbf{M}_{kjmn}\nabla_i\mathbf{M}_{mn}$$
$$-\mathbf{M}_{jkmn}\nabla_k\nabla_i\mathbf{M}_{mn}+\nabla_k\mathbf{M}_{mn}\nabla_i\mathbf{M}_{4kjmn}$$
$$\left.-\mathbf{M}_{mn}\nabla_l\nabla_i\mathbf{M}_{4jlmn})]\right\}. \quad \text{(B10)}$$

The elastic stress corresponding to the free energy F_{lcp} is identified as

$$\tau_{lcp}^e = -\langle\mathbf{m}\times\mathcal{R}(\mu_a^{(1)})\mathbf{m}\rangle+\frac{C_1kT\mathcal{L}^2}{32}[\nabla\Phi\nabla\Phi-\Phi\nabla\nabla\Phi]$$
$$+\frac{C_1kTl^2}{64}[\nabla\Phi\nabla\cdot\mathbf{M}-\nabla\nabla\Phi\cdot\mathbf{M}+\nabla_i\mathbf{M}_{\alpha j}\nabla_\alpha\Phi$$
$$-\nabla_\alpha\nabla_i\mathbf{M}_{j\alpha}\Phi]-\frac{\beta C_1kT\mathcal{L}^2}{32}[\nabla_i\mathbf{M}_{kl}\nabla_j\mathbf{M}_{kl}-(\nabla\nabla\mathbf{M}):\mathbf{M}]$$
$$+\frac{\beta C_1kTL^2}{64}[\nabla_i\nabla_k\mathbf{M}_{mn}\mathbf{M}_{4,jkmn}+(\nabla_i\nabla_k\cdot\mathbf{M}_{4,kjmn})\mathbf{M}_{mn}$$
$$-\nabla_i\mathbf{M}_{mn}(\nabla_k\mathbf{M}_{4,kjmn})-\nabla_k\mathbf{M}_{4,kjmn}\nabla_i\mathbf{M}_{mn}]. \quad \text{(B11)}$$

For the approximate theory, we only need to derive the stress corresponding to the interaction potential. The approximate form of the interaction potential is

$$F_{int}^{(a)} = kT\chi\left\langle\int_\Omega\left(\phi(\mathbf{x},t)+\frac{L^2}{24}\nabla\nabla\phi:\mathbf{mm}\right)d\mathbf{x}\right\rangle. \quad \text{(B12)}$$

The variation of the free energy with respect to f is

$$\delta F_{int}^{(a)} = kT\chi L \int_\Omega \int_{\|\mathbf{m}\|=1} \left(\phi(\mathbf{x},t) + \frac{L^2}{24} \nabla\nabla\phi:\mathbf{mm} \right) \delta f + \left(\delta\phi + \frac{L^2}{24} \delta\nabla\nabla\phi:\mathbf{mm} \right) f d\mathbf{m} d\mathbf{x}$$
$$= \frac{L^2}{24} kT\chi \int_\Omega \mathbf{K}_{\alpha\beta} (\nabla\nabla\phi\cdot\mathbf{M} + \mathbf{M}\cdot\nabla\nabla\phi - 2\nabla\nabla\phi:\mathbf{M}_4)_{\alpha\beta} + \nabla_\alpha\phi\nabla_i\mathbf{M}_{i\beta} - \nabla_i\nabla_\alpha\phi\mathbf{M}_{\beta i}$$
$$= \int_\Omega \mathbf{K}_{\alpha\beta} \left[-\langle \mathbf{m}\times\mathcal{R}\mu_a^{(2)}\mathbf{m}\rangle_{\alpha\beta} + \frac{L^2}{24} kT\chi [\nabla_\alpha\phi\nabla_i\mathbf{M}_{i\beta} - \nabla_i\nabla_\alpha\phi\mathbf{M}_{\beta i}] \right], \tag{B13}$$

where

$$\mu_a^{(2)} = \left(1 + \frac{L^2}{24} \mathbf{mm}:\nabla\nabla \right) \phi. \tag{B14}$$

The corresponding stress tensor is given by

$$(\tau_{int}^e)_{\alpha\beta} = -\langle \mathbf{m}\times\mathcal{R}\mu_a^{(2)}\mathbf{m}\rangle_{\alpha\beta} + \frac{L^2}{24} kT\chi [\nabla_\alpha\phi\nabla_i\mathbf{M}_{i\beta} - \nabla_i\nabla_\alpha\phi\mathbf{M}_{\beta i}]$$
$$= \frac{L^2}{24} kT\chi (\nabla\nabla\phi\cdot\mathbf{M} + \mathbf{M}\cdot\nabla\nabla\phi - 2\nabla\nabla\phi:\mathbf{M}_4)_{\alpha\beta} + \nabla_\alpha\phi\nabla_i\mathbf{M}_{i\beta} - \nabla_i\nabla_\alpha\phi\mathbf{M}_{\beta i}. \tag{B15}$$

The first three terms belong to the terms derived from the chemical potential and the last two terms are the extra terms due to the spatial convection and spatial inhomogeneity.

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