PHYSICAL REVIEW E, VOLUME 65, 051504

Kinetic theory for flows of nonhomogeneous rodlike liquid crystalline polymers with a nonlocal intermolecular potential

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(Received 13 September 2001; revised manuscript received 11 January 2002; published 13 May 2002)

The Doi kinetic theory for flows of homogeneous, rodlike liquid crystalline polymers (LCPs) is extended to model flows of nonhomogeneous, rodlike LCPs through a nonlocal (long-range) intermolecular potential. The theory features (i) a nonlocal, anisotropic, effective intermolecular potential in an integral form that is consistent with the chemical potential, (ii) short-range elasticity as well as long-range isotropic and anisotropic elasticity, (iii) a closed-form stress expression accounting for the nonlocal molecular interaction, and (iv) an extra elastic body force exclusively associated with the integral form of the intermolecular potential. With the effective intermolecular potential, the theory is proven to be well posed in that it warrants a positive entropy production and thereby the second law of thermodynamics. Approximate theories are obtained by gradient expansions of the number density function in the free energy density.

DOI: 10.1103/PhysRevE.65.051504 PACS number(s): 61.30.Vx, 61.30.Cz, 61.25.Hq, 61.30.Dk

I. INTRODUCTION

Doi developed his well-known kinetic theory for spatially homogeneous flows of rodlike liquid crystalline polymers (LCPs), in which the excluded volume effect is accounted for using either the Onsager or Maier-Saupe potential [1]. Later, Doi, Shimada, and Okano extended the theory to model flows of nonhomogeneous LCPs by introducing a long-range intermolecular potential, called the hard-rod potential, through a mean field calculation [2]. With the extended Doi theory, Shimada, Doi, and Okano [3] analyzed the spinodal decomposition kinetics. Marrucci and Greco [4] further improved the extended Doi theory by incorporating the molecular anisotropy and the range of interaction into the theory and approximated the nonlocal potential using a truncated Taylor series expansion of the probability density function (PDF) to obtain an approximate potential depending on gradients of the second moments of the PDF. In the Marrucci-Greco intermolecular potential, both long-range isotropic and anisotropic elasticity are accounted for. Using the approximate theory, Marrucci and Greco [4] derived the explicit formula for the three Frank elastic constants (elastic moduli) K_1, K_2, and K_3 and identified their relative numerical order. Later, Bhave analyzed the spinodal decomposition kinetics of the approximate Marrucci-Greco theory and compared them with the results obtained from the extended Doi theory [5]. However, the impact of the intermolecular potentials with gradients of the PDF function was not fully accounted for in the stress expression in subsequent use of the theories until Feng, Sgalary, and Leal [6] showed that the stress should be augmented by additional elastic stress terms for the one-constant approximation of the Marrucci-Greco potential recently, which accounts for only the long-range isotropic elasticity in the theory. Recently, Wang [7], extended the theories to model flows of spheroidal LCP molecules with rodlike and disklike LCPs as two extreme limits, in which an effective intermolecular potential resulting from a gradient expansion of a nonlocal intermolecular potential is derived and used in the Smoluchowski equation to ensure the second law of thermodynamics, an important thermodynamical property that the Marrucci-Greco theory does not share. Furthermore, he derived a closed-form expression for the stress tensor extending the work of Feng, Sgalary, and Leal to include the long-range anisotropic elasticity given in the intermolecular potential. None of the theories mentioned above addresses the effect of the truely nonlocal intermolecular interaction on the elastic stress and the well posedness of the hydrodynamic theory though.

The approximate theories based on the Taylor expansion of the PDF are easier to handle theoretically, especially, for deriving the constitutive equation in differential forms for the orientation tensor since their intermolecular potentials only contain local gradients of the PDF. However, it has no advantages for Brownian dynamical simulation on the Smoluchowski equation or its equivalent stochastic equations for the dynamical variables because an ensemble-averaged stress expression would have to be evaluated if the coupled hydrodynamic equations were solved. Moreover, they are long-wave, weakly nonlocal approximations to the kinetic theories

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of nonlocal intermolecular potentials after all. In fact, most are truncated at the quadratic order.

The purpose of this paper is to provide a general framework for the systematic development of the Smoluchowski equation with a nonlocal intermolecular potential and the derivation of the stress expression, which gives the critical coupling between the macroscopic momentum transport and the microscopic molecular orientation, and to explore the well posedness of the hydrodynamic theory in terms of energy dissipation. The development begins with generalizing the free energy given in the Doi kinetic theory for homogeneous LCPs to account for nonlocal interactions and the LCP molecular anisotropy following Marrucci and Greco's approach [4], but in a more general formalism. We adopt a number density function (NDF) in place of the PDF for the potentially spatial variation of the orientational distribution of the LCP molecules in the presence of translational diffusion. We then identify an effective intermolecular potential in accordance with the variational principle in the definition of the chemical potential. The chemical potential comprised of the effective intermolecular potential is then used to yield the Smoluchowski or kinetic equation. With the kinetic equation, we set out to derive the elastic stress in closed form. Due to the nonlocality in the chemical potential, however, an extra elastic body force in addition to the elastic stress emerges, which would vanish otherwise. We then show that the theory developed warrants a positive entropy production thereby the second law of thermodynamics. Finally, we outline the procedure for the derivation of a weakly nonlocal approximate theory via gradient expansions of the NDF and refer the readers to Ref. [7] for details.

II. INTERMOLECULAR POTENTIAL

We model the molecules of the LCP as rigid rods (cylinders of uniform circular cross sections whose height is considerably larger than its cross-sectional diameter) of equal size. Let Ω be a material volume in which the solution of LCPs resides and $f(\mathbf{m},\mathbf{x},t)$ the NDF of liquid crystalline polymers parallel to direction $\mathbf{m}$ at material point $\mathbf{x}$ and time t. For the LCP system, we extend the free energy in the Doi kinetic theory [1] to include a nonlocal intermolecular potential as follows:

$$A[f]=kT\int_{\Omega}\int_{\|\mathbf{m}\|=1}\bigg[f(\mathbf{m},\mathbf{x},t)\ln f(\mathbf{m},\mathbf{x},t)-f(\mathbf{m},\mathbf{x},t)+\frac{1}{2kT}U(\mathbf{m},\mathbf{x},t)f(\mathbf{m},\mathbf{x},t)\bigg]d\mathbf{m}\,d\mathbf{x}, \tag{1}$$

where k is the Boltzmann constant and T the absolute temperature; the intermolecular potential $U(x,\mathbf{m},t)$ is defined by

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

Here

$$B(\mathbf{m},\mathbf{m}',\mathbf{x})=\begin{cases}\dfrac{N}{V[\mathbf{B}(0,R)]}\|\mathbf{m}\times\mathbf{m}'\|, & \mathbf{x}\in\mathbf{B}(0,R),\\ 0 \quad \text{otherwise,}\end{cases} \tag{3}$$

defines the range of intermolecular interaction and the size of the excluded volume. It is symmetric with respect to $\mathbf{m}$ and $\mathbf{m}'$. [Here we choose the range of the interaction as a spherical ball $\mathbf{B}(0,R)\in R^3$, a more general domain can be chosen in other applications.] N measures the strength of the intermolecular potential. $V[\mathbf{B}(0,R)]$ is the volume of $\mathbf{B}(0,R)$.

$$H(\mathbf{m},\mathbf{x})=\begin{cases}\dfrac{1}{V[S(0)]}, & \mathbf{x}\in S(0),\\ 0 \quad \text{otherwise,}\end{cases} \tag{4}$$

is the normalized characteristic function for the domain occupied by the LCP molecule, called the shape function, $S(0)$ is the domain occupied by the molecule with its center of mass at the origin, and $V[S(0)]$ is the volume of $S(0)$. This intermolecular potential is quite general in that it can be used to account for a variety of molecular geometries of revolutionary configurations by specifying the shape function H and the excluded volume formula in B. For noncylindrical shapes, the excluded volume formula would have to be modified accordingly. The intermolecular potential used by Marrucci and Greco [4] and Wang [7] are two special cases. Since we are interested in the rodlike LCP here, H is chosen as a normalized characteristic function of a cylinder, representing the rodlike molecular configuration. We remark that both $B(\mathbf{m},\mathbf{m}',\mathbf{x})$ and $H(\mathbf{m},\mathbf{x})$ can be chosen to be smooth functions with compact support to facilitate numerical computations and mathematical analyses if it is necessary. By definition, the number density of the LCP at material point $\mathbf{x}$ is given by

$$\int_{\|\mathbf{m}\|=1}f(\mathbf{m},\mathbf{x},t)d\mathbf{m}. \tag{5}$$

The intermolecular potential is essentially an averaged excluded volume with respect to the NDF over the domain occupied by the single LCP molecule and the range of molecular interaction whose size is to be determined by experiments. This choice of intermolecular potential takes into account the anisotropy of each individual molecule (via H) as well as the anisotropy in their ensemble at the material point $\mathbf{x}$ (via BH and f). It thus exerts an anisotropic mean field of both isotropic and anisotropic elasticity to the LCP molecule, an attribute of anisotropic microstructure materials like LCPs.

By definition, the chemical potential is the variation of the free energy with respect to the NDF

$$\mu=\frac{\delta A}{\delta f}. \tag{6}$$

A simple calculation aided by changing the order of integration leads to

$$\mu = kT \ln f + \tfrac{1}{2}(U + U_2), \tag{7}$$

where

$$U_2(\mathbf{m},\mathbf{x},t) = kT \int_{\|\mathbf{m}'\|=1} \int_{\Omega^2} B(\mathbf{m}',\mathbf{m},\mathbf{x}''-\mathbf{x}') \times H(\mathbf{m},\mathbf{x}'-\mathbf{x}) f(\mathbf{m},\mathbf{x}'',t)\, d\mathbf{x}''\, d\mathbf{x}'\, d\mathbf{m}'. \tag{8}$$

We identify the second part of the chemical potential

$$U_e = \frac{1}{2}(U + U_2) \tag{9}$$

as the effective intermolecular potential since the total bulk free energy is unchanged if the intermolecular potential is replaced by the effective intermolecular potential and it is clearly the variation of the free energy corresponding to the molecular interaction

$$U_e = \frac{\delta}{\delta f}\left[\frac{1}{2}\int_{\Omega}\int_{\|\mathbf{m}\|=1} U(\mathbf{m},\mathbf{x},t) f(\mathbf{m},\mathbf{x},t)\, d\mathbf{m}\, d\mathbf{x}\right]. \tag{10}$$

The form of the effective intermolecular potential is then required by the variational principle. Mathematically, this is equivalent to a symmetrization of the intermolecular potential. Although the effective intermolecular potential and U contribute equally to the free energy, they are different as functions of $\mathbf{m}$ and $\mathbf{x}$ in that the mean fields corresponding to the two potentials differ slightly. Furthermore, the kernel function

$$\int_{\Omega}\int_{\|\mathbf{m}'\|=1} \tfrac{1}{2}\,[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x}) H(\mathbf{m}',\mathbf{x}''-\mathbf{x}') + B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'') H(\mathbf{m},\mathbf{x}-\mathbf{x}')]\, d\mathbf{m}'\, d\mathbf{x}' \tag{11}$$

in the free energy with the effective potential is independent of the pair of double $(\mathbf{m},\mathbf{x})$ and $(\mathbf{m}',\mathbf{x}'')$, namely, it is indifferent to the choice of the test molecule and its location, making the effective potential an ideal choice for the intermolecular potential. This latter property is trivially satisfied in the Doi kinetic theory by the way; it becomes a nontrivial issue in the kinetic theories with nonlocal intermolecular potentials however. The use of the effective intermolecular potential seems straightforward, but was overlooked by many before. In fact, it is crucial for the development of a well-posed hydrodynamic theory since it warrants the positive entropy production and thereby the second law of the thermodynamics as we will show next.

III. SMOLUCHOWSKI EQUATION

Having decided upon the intermolecular potential, we next derive the Smoluchowski (kinetic) equation for the NDF. We treat the LCP material system as incompressible and adopt the effective intermolecular potential (9). Accounting for both the translational and rotational diffusion as well as convection and following the derivation given in Refs. [1,7], we present the Smoluchowski equation for the LCP system as follows:

$$\frac{df}{dt} = \frac{1}{kT}\nabla\cdot\{[D_{\|}\mathbf{mm} + D_{\perp}(\mathbf{I}-\mathbf{mm})]\cdot(\nabla\mu) f\} + \frac{1}{kT}\boldsymbol{\mathcal{R}}\cdot[D_r(\mathbf{m}) f \boldsymbol{\mathcal{R}}\mu] - \boldsymbol{\mathcal{R}}\cdot[\mathbf{m}\times\dot{\mathbf{m}} f],$$

$$\dot{\mathbf{m}} = K\cdot\mathbf{m} - K{:}\mathbf{mmm}, \tag{12}$$

where $D_{\|} \geqslant 0$ and $D_{\perp} \geqslant 0$ are the translational diffusion coefficients parallel and normal to the orientation of the LCP molecule, respectively, $D_r(\mathbf{m}) \geqslant 0$ is the rotary diffusivity [1], ∇ is the gradient operator with respect to the spatial variable $\mathbf{x}$, $\nabla_{\mathbf{m}}$ is the gradient operator with respect to the rotational variable $\mathbf{m}$, $\boldsymbol{\mathcal{R}} = \mathbf{m}\times\nabla_{\mathbf{m}}$ the rotational gradient operator [8], $K = \nabla\mathbf{v}$ is the velocity gradient tensor, and d/dt the material derivative $(\partial/\partial t) + \mathbf{v}\cdot\nabla$.

This equation, also known as the kinetic equation, governs the time evolution of the number density function $f(\mathbf{m},\mathbf{x},t)$. Since μ depends on f nonlocally, the kinetic equation is in fact an integral-differential equation. With the time evolutionary equation for the NDF, we next derive an expression for the stress tensor from a virtual work principle to couple the orientational dynamics of LCPs to the momentum transport process.

IV. CONSTITUTIVE EQUATION FOR THE STRESS TENSOR

In the LCP system, the extra stress is given by two parts, the viscous stress τ_s and the elastic stress τ_e,

$$\tau = \tau_s + \tau_e. \tag{13}$$

For solutions of LCPs the viscous stress comes from two sources, one from the solvent and the other from the solvent-LCP interaction derived in [1]

$$\tau_s = 2\eta_s\mathbf{D} + 2kT\zeta\mathbf{D}{:}\langle\mathbf{mmmm}\rangle, \tag{14}$$

where $\mathbf{D} = \frac{1}{2}(\nabla\mathbf{v} + \nabla\mathbf{v}^T)$ is the strain rate tensor, η_s is the solvent viscosity, ζ is a friction coefficient, both of which are positive, and

$$\langle(\cdot)\rangle = \int_{\|\mathbf{m}\|=1} (\cdot) f(\mathbf{m},\mathbf{x},t)\, d\mathbf{m} \tag{15}$$

is an ensemble average with respect to the NDF $f(\mathbf{m},\mathbf{x},t)$.

The elastic stress is derived through a generalized virtual work principle [1,6]. 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 over the control volume Ω in response to the infinitesimal deformation and displacement can be identified through the work done by the elastic body force along the displacement and the elastic stress with respect to the deformation rate. It then follows that

$$\delta A = \int_{\Omega} (\delta\epsilon{:}\tau_e - \delta\mathbf{u}\cdot\mathbf{F}_e)\, d\mathbf{x}, \tag{16}$$

where F_e is the body force induced by the long-range (i.e., nonlocal) molecular interaction given by

$$= -\frac{kT}{4}\left\langle\left\langle \int_{\Omega^2} f(\mathbf{m},\mathbf{x},t)\boldsymbol{\nabla}\left[\frac{1}{f}[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x}) \times H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'') \times H(\mathbf{m},\mathbf{x}-\mathbf{x}')]\right]dx'\,d\mathbf{x}''\right\rangle\right\rangle. \tag{17}$$

The elastic stress is identified as

$$\tau_e = -\langle \mathbf{m}\times\mathcal{R}\mu\mathbf{m}\rangle. \tag{18}$$

The details of the derivation are given in the appendix.

From Eq. (17) and the derivation presented in the appendix, we conclude that the extra elastic body force is the direct consequence of the nonlocality in the effective intermolecular potential. Equation (17) shows explicit dependence on the spatial inhomogeneity of the NDF as well as the spatial variation of the interaction intensity quantified by *BH*. Thus, the specific expression of the extra elastic body force depends strongly on the form of the nonlocal intermolecular potential [9].

The elastic stress yields a torque to the macroscopic motion given by the ensemble-averaged molecular torque:

$$-\tau_{ij}\epsilon_{ijk} = \langle \mathcal{R}\mu\rangle_k, \tag{19}$$

where ϵ_{ijk} is the permutation symbol [8]. An additional torque comes from the extra elastic body force. The total torque on the control volume is then given by

$$\int_\Omega(-\tau_{ij}\epsilon_{ijk}+\mathbf{x}_i\mathbf{F}_{ej}\epsilon_{ijk})d\mathbf{x} = \int_\Omega\left(\int_{\|\mathbf{m}\|=1}(\mathcal{R}\mu)_k f(\mathbf{m},\mathbf{x},t)d\mathbf{m}+\mathbf{x}_i\mathbf{F}_{ej}\epsilon_{ijk}\right)d\mathbf{x}. \tag{20}$$

The Smoluchowski equation, the constitutive equation of stress and the extra body force along with the continuity equation and balance of linear momentum constitute the governing system of equations for the solution of rodlike LCPs. The continuity equation is

$$\dot{\rho}=0 \tag{21}$$

where ρ is the mass density of the LCP solution. The balance of linear momentum equation is

$$\rho\dot{\mathbf{v}} = \boldsymbol{\nabla}\cdot(-p\mathbf{I}+\tau)+\mathbf{F}_e+\rho\mathbf{g}, \tag{22}$$

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

Given the hydrodynamic theory, we next examine the time evolution of the total energy in the system.

V. ENTROPY PRODUCTION AND ENERGY DISSIPATION

Let S be the entropy of the LCP system in Ω. When the external force is neglected, the entropy production of an isothermal system can be calculated as [10]

$$\begin{aligned} T\dot{S} &= -\frac{d}{dt}\left[\int_\Omega(\tfrac{1}{2}\rho\mathbf{v}\cdot\mathbf{v})d\mathbf{x}+A[f]\right] \\ &= -\int_\Omega\rho\frac{d\mathbf{v}}{dt}\cdot\mathbf{v}\,d\mathbf{x} \\ &\quad -kT\int_\Omega\int_{\|\mathbf{m}\|=1}\frac{d}{dt}\left[f(\mathbf{m},\mathbf{x},t)\ln f(\mathbf{m},\mathbf{x},t)-f(\mathbf{m},\mathbf{x},t) + \frac{1}{2kT}U_e(\mathbf{m},\mathbf{x},t)f(\mathbf{m},\mathbf{x},t)\right]d\mathbf{m}\,d\mathbf{x} \\ &= -\int_\Omega[\boldsymbol{\nabla}\cdot(-p\mathbf{I}+\tau_s+\tau_e)+\mathbf{F}_e]\cdot\mathbf{v}\,d\mathbf{x} \\ &\quad -kT\int_\Omega\int_{\|\mathbf{m}\|=1}\frac{d}{dt}\left[f(\mathbf{m},\mathbf{x},t)\ln f(\mathbf{m},\mathbf{x},t)-f(\mathbf{m},\mathbf{x},t) + \frac{1}{2kT}U_e(\mathbf{m},\mathbf{x},t)f(\mathbf{m},\mathbf{x},t)\right]d\mathbf{m}\,d\mathbf{x} \\ &= \int_\Omega[(-p\mathbf{I}+\tau_s+\tau_e):\boldsymbol{\nabla}\mathbf{v}-\mathbf{F}_e\cdot\mathbf{v}]d\mathbf{x} \\ &\quad -kT\int_\Omega\int_{\|\mathbf{m}\|=1}\frac{d}{dt}\left[f(\mathbf{m},\mathbf{x},t)\ln f(\mathbf{m},\mathbf{x},t)-f(\mathbf{m},\mathbf{x},t) + \frac{1}{2kT}U_e(\mathbf{m},\mathbf{x},t)f(\mathbf{m},\mathbf{x},t)\right]d\mathbf{m}\,d\mathbf{x} \\ &= \int_\Omega\tau_s:\boldsymbol{\nabla}\mathbf{v}d\mathbf{x}-\int_\Omega\int_{\|\mathbf{m}\|=1}\mu\frac{d^*}{dt}f(\mathbf{m},\mathbf{x},t)d\mathbf{m}\,d\mathbf{x} \\ &= \int_\Omega[2\eta_s\mathbf{D}:\mathbf{D}+2kT\zeta\langle(\mathbf{mm}:\mathbf{D})^2\rangle]d\mathbf{x} \\ &\quad +\frac{1}{kT}\int_\Omega\langle\boldsymbol{\nabla}(\mu)\cdot[D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm})]\cdot\boldsymbol{\nabla}\mu + \mathcal{R}\mu\cdot D_r\mathcal{R}\mu\rangle d\mathbf{x}, \end{aligned} \tag{23}$$

where

$$\frac{d^*}{dt} = \frac{1}{kT}\boldsymbol{\nabla}\cdot\{[D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm})]\cdot(\boldsymbol{\nabla}\mu)f\} + \frac{1}{kT}\mathcal{R}\cdot[D_r(\mathbf{m})f\mathcal{R}\mu]. \tag{24}$$

This is non-negative definite provided

$$\begin{gathered} \eta_s\geqslant 0,\zeta\geqslant 0, \\ D_\parallel\mathbf{mm}+D_\perp(\mathbf{I}-\mathbf{mm})\geqslant 0, \\ D_r(\mathbf{m})\geqslant 0. \end{gathered} \tag{25}$$

Thus, the total energy is dissipative and the second law of thermodynamics is verified under the isothermal condition since Eqs. (25) are all positive by assumption. We remark that the second law of thermodynamics is warranted because of the choice of the effective intermolecular potential. If the original intermolecular potential $U(\mathbf{m},\mathbf{x},t)$ was used in the Smoluchowski equation, the above inequality could not have been established.

VI. APPROXIMATE THEORIES BASED ON GRADIENT EXPANSIONS OF NDF

An approximate, ''weakly nonlocal'' theory of an intermolecular potential in differential forms can be obtained if we expand the NDF in Taylor series in the free energy density (1). An approximate theory with a quadratic expansion has been derived for flows of nonhomogeneous LCPs of spheroidal configurations in Ref. [7], where an effective intermolecular potential is devised at the level of second and fourth order moments of NDF. Higher order truncation may also be attempted through straightforward, but laborious calculations if one would like to pursue higher order of accuracy in the approximation to the integral form of intermolecular potential.

As illustrated in Ref. [7], the derivation of the approximate theories should share the same procedures as we outlined above, i.e., an effective intermolecular potential must be used in the Smoluchowski equation to be consistent with the chemical potential and to warrant the positive entropy production in the total energy. Moreover, special care must be exercised in the derivation of the elastic stress when applying the generalized virtual work principle [6]. In the approximate theories, the extra elastic body force reduces to a divergence of a second order tensor so that it can be combined completely with the elastic stress given by Eq. (18) to give the total elastic stress tensor. For details, please refer to Ref. [7].

VII. CONCLUSION

We have outlined a systematic extension of the Doi kinetic theory to a kinetic theory of nonlocal intermolecular potential of an integral form for solutions of nonhomogeneous, rodlike liquid crystalline polymers, in which both short-range elasticity and long-range isotropic as well as anisotropic elasticity are included. In this development, we have identified the need for an effective intermolecular potential to be consistent with the chemical potential and to ensure the second law of thermodynamics. In the presence of the nonlocal intermolecular potential of the integral form, we discover an extra elastic body force that exerts an additional elastic body torque at each material point besides the ensemble-averaged molecular torque. The existence of the extra elastic body force is due to the nonlocality in the intermolecular potential involving the finite range of molecular interaction and the spatial variation of the NDF.

This theory generalizes all existing kinetic-based hydrodynamic theories for solutions of rodlike LCPs and has the potential to accommodate an extended class of molecular configurations, for example, the LCP molecules of revolutionary symmetry, although we present it here only for rodlike LCPs. It provides the critical coupling between the macroscopic momentum transport and the mesoscopic material structure through the closed-form stress and extra elastic body force formula. The positive entropy production clearly establishes the dissipative nature of the theory under the isothermal condition. It is therefore proven to be a hydrodynamically well-posed theory for studying the flow behavior of nonhomogeneous rodlike LCPs. The stress and the extra elastic body force formula will also be useful if the hydrodynamic simulation is carried out with the equivalent stochastic differential equations instead of the Smoluchowski equation.

Approximate theories can be obtained by gradient expansions of the NDF in the free energy density. The resultant has a chemical potential that depends on derivatives of the first few moments of the NDF. A symmetrized effective intermolecular potential must be devised in consistence with the chemical potential to ensure the second law of thermodynamics. Different from the nonlocal theory though, it yields a stress expression whose divergence provides all the elastic forces.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial assistance provided by the Morningside Center, Academia Sinica, where the work was initiated while participating in the summer program on multiscale modeling of complex fluids. Q.W. was partially supported through an AFOSR Grant No. F49620-99-1-0003, W.E was partially supported by an ONR Grant No. N00014-01-1-0674. The work of C.L. was partially supported by a NSF Grant No. DMS-9972040, and P.Z. was partially supported by Special Funds for Major State Basic Research Projects of China G1999032804.

APPENDIX: DERIVATION OF THE ELASTIC STRESS AND BODY FORCE

We derive the elastic stress and the extra elastic body force using the virtual *work principle* [1], which is also equivalent to the *least action principle* [11]. We begin with an infinitesimal deformation given by $\epsilon = K\delta t$. The corresponding variation of the NDF f is given by the change of f along the material point path given by [1]

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

The virtual work principle states that the change of the free energy is equal to the virtual work done by the elastic stress τ with respect to the infinitesimal deformation and the extra elastic body force $\mathbf{F}_e$ along the infinitesimal displacement $\delta u = \mathbf{v}\delta t$,

$$\delta A = \int_{\Omega}[\tau_e : K - \mathbf{F}_e\cdot\mathbf{v}]d\mathbf{x}\,\delta t. \tag{A2}$$

Here,

$$\begin{aligned}\delta A &= kT\int_{\Omega}\int_{\|\mathbf{m}\|=1}\delta\left[f\ln f-f+\frac{1}{2kT}(U_e)f\right]d\mathbf{m}\,d\mathbf{x}\\
&= kT\int_{\Omega}\int_{\|\mathbf{m}\|=1}\left\{\left[\ln f+\frac{U_e}{kT}\right]\delta f\right.\\
&\quad\left.+\left[\frac{1}{2kT}\,\delta(U_e)f-\frac{1}{2kT}(U_e)\,\delta f\right]\right\}d\mathbf{m}\,d\mathbf{x}\\
&= kT\int_{\Omega}\int_{\|\mathbf{m}\|=1}\left[\left[\ln f+\frac{U_e}{kT}\right]\frac{df}{dt}\,\delta t\right.\\
&\quad\left.+\left(\frac{1}{2kT}\,\delta(U_e)f-\frac{1}{2kT}(U_e)\,\frac{df}{dt}\,\delta t\right)\right]d\mathbf{m}\,d\mathbf{x}\\
&= kT\int_{\Omega}\int_{\|\mathbf{m}\|=1}\left[\mu\,\frac{df}{dt}\,\delta t\right.\\
&\quad\left.+\left(\frac{1}{2kT}\,\delta U_e f-\frac{1}{2kT}\,U_e\frac{df}{dt}\,\delta t\right)\right]d\mathbf{m}\,d\mathbf{x},\end{aligned}\tag{A3}$$

where the incompressibility condition is used in moving the derivative into the integral. The first term on the right-hand side can be rewritten as

$$\begin{aligned}&\int_{\Omega}\int_{\|\mathbf{m}\|=1}\mu\,\delta f\,d\mathbf{m}\,d\mathbf{x}\\
&\quad=\int_{\Omega}\int_{\|\mathbf{m}\|=1}\mu[-\boldsymbol{\mathcal{R}}\cdot(\mathbf{m}\times K\boldsymbol{\cdot}\mathbf{m}f)]d\mathbf{m}\,d\mathbf{x}\,\delta t\\
&\quad=\int_{\Omega}\int_{\|\mathbf{m}\|=1}\boldsymbol{\mathcal{R}}\mu(\mathbf{m}\times K\boldsymbol{\cdot}\mathbf{m})f\,d\mathbf{m}\,d\mathbf{x}\,\delta t\\
&\quad=-\int_{\Omega}\int_{\|\mathbf{m}\|=1}(\mathbf{m}\times\boldsymbol{\mathcal{R}}\mu\mathbf{m}):Kf\,d\mathbf{m}\,d\mathbf{x}\,\delta t.\end{aligned}\tag{A4}$$

The elastic stress can then be identified as

$$\tau_e=-\langle\mathbf{m}\times\boldsymbol{\mathcal{R}}\mu\mathbf{m}\rangle.\tag{A5}$$

The second part of the right-hand side reads:

$$\begin{aligned}&\int_{\Omega}\int_{\|\mathbf{m}\|=1}\left(\frac{1}{2}\,\delta U_e f-\frac{1}{2}\,U_e\frac{df}{dt}\,\delta t\right)d\mathbf{m}\,d\mathbf{x}\\
&=\int_{\Omega}\int_{\|\mathbf{m}\|=1}\left(\frac{1}{2}\,\frac{dU_e}{dt}\,f-\frac{1}{2}\,U_e\frac{df}{dt}\right)d\mathbf{m}\,d\mathbf{x}\,\delta t\\
&=\frac{kT}{4}\left[\int_{\Omega^3}d\mathbf{x}\int_{\|\mathbf{m}\|=1}d\mathbf{m}\,f(\mathbf{m},\mathbf{x},t)\int_{\|\mathbf{m}'\|=1}d\mathbf{m}'\frac{d}{dt}\right.\\
&\quad\times\{[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')\\
&\quad+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]f(\mathbf{m}',\mathbf{x}'',t)\}d\mathbf{x}''d\mathbf{x}'\\
&\quad\left.-\int_{\Omega}\int_{\|\mathbf{m}\|=1}U_e\frac{df}{dt}\,d\mathbf{m}\,d\mathbf{x}\right]\delta t\\
&=\frac{kT}{4}\left[\int_{\Omega^3}d\mathbf{x}\int_{\|\mathbf{m}\|=1}d\mathbf{m}\,f(\mathbf{m},\mathbf{x},t)\int_{\|\mathbf{m}'\|=1}d\mathbf{m}'\right.\\
&\quad\times\left\{v(\mathbf{x},t)\cdot\boldsymbol{\nabla}[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')\right.\\
&\quad+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]f(\mathbf{m}',\mathbf{x}'',t)\\
&\quad+[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')\\
&\quad+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]\\
&\quad\left.\left.\times\frac{\partial}{\partial t}f(\mathbf{m}',\mathbf{x}'',t)\right\}dx''dx'-\int_{\Omega}\int_{\|\mathbf{m}\|=1}U_e\frac{df}{dt}\,d\mathbf{m}\,d\mathbf{x}\right]\delta t\\
&=(\mathrm{I})+(\mathrm{II}),\end{aligned}\tag{A6}$$

where

$$\begin{aligned}(\mathrm{I})&=\frac{kT}{4}\int_{\Omega^3}\int_{\|\mathbf{m}\|=1}\int_{\|\mathbf{m}'\|=1}\mathbf{v}(\mathbf{x},t)\cdot\boldsymbol{\nabla}[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})\\
&\quad\times H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]\\
&\quad\times f(\mathbf{m},\mathbf{x},t)f(\mathbf{m}',\mathbf{x}'',t)d\mathbf{x}''d\mathbf{x}'\,d\mathbf{m}'\,d\mathbf{m}\,d\mathbf{x}\,\delta t\\
&=\frac{kT}{4}\int_{\Omega}\mathbf{v}(\mathbf{x},t)\cdot\left\langle\left\langle\int_{\Omega^2}\boldsymbol{\nabla}[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})\right.\right.\\
&\quad\times H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')\\
&\quad\left.\left.\times H(\mathbf{m},\mathbf{x}-\mathbf{x}')]d\mathbf{x}''d\mathbf{x}'\right\rangle\right\rangle d\mathbf{x}\,\delta t\end{aligned}\tag{A7}$$

and

$$\begin{aligned}(\mathrm{II})&=\frac{kT}{4}\left[\int_{\Omega^3}d\mathbf{x}\int_{\|\mathbf{m}\|=1}d\mathbf{m}\,d\mathbf{x}'\,d\mathbf{x}''d\mathbf{x}\int_{\|\mathbf{m}'\|=1}d\mathbf{m}'\,f(\mathbf{m},\mathbf{x},t)\right.\\
&\quad\times[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}'-\mathbf{x})\\
&\quad+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]\\
&\quad\times\left(\frac{d}{dt}f(\mathbf{m}',\mathbf{x}'',t)-\mathbf{v}(\mathbf{x}'',t)\cdot\boldsymbol{\nabla}_{\mathbf{x}''}f(\mathbf{m}',\mathbf{x}'',t)\right)\delta t\\
&\quad\left.-\int_{\Omega}\int_{\|\mathbf{m}\|=1}U_e\frac{df}{dt}\,d\mathbf{m}\,d\mathbf{x}\right]\delta t.\end{aligned}\tag{A8}$$

Exchanging the order of integration, we notice that the first and the third term cancel each other. In the end, we have

$$
\begin{aligned}
(\mathrm{II}) = & -\frac{kT}{4}\int_{\Omega^3}\int_{\|\mathbf{m}\|=1}\int_{\|\mathbf{m}'\|=1}\mathbf{v}(\mathbf{x},t)\cdot\boldsymbol{\nabla} f(\mathbf{m},\mathbf{x},t)\\
& \times[B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')\\
& +B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]\\
& \times f(\mathbf{m}',\mathbf{x}'',t)f(\mathbf{m},\mathbf{x},t)\,d\mathbf{x}''d\mathbf{x}'\,d\mathbf{m}'\,d\mathbf{m}\,d\mathbf{x}\;\delta t\\
= & -\frac{kT}{4}\int_{\Omega}\mathbf{v}(\mathbf{x},t)\cdot\left\langle\left\langle\int_{\Omega^2}\boldsymbol{\nabla}[\ln f(\mathbf{m},\mathbf{x},t)]\right.\right.\\
& \times[B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')\\
& \left.\left.+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]d\mathbf{x}''d\mathbf{x}'\right\rangle\right\rangle d\mathbf{x}\;\delta t.
\end{aligned}
\tag{A9}
$$

Combining (I) and (II), we identify the extra elastic body force as

$$
\begin{aligned}
\mathbf{F}_e = & -\frac{kT}{4}\left[\left\langle\left\langle\int_{\Omega^2}\boldsymbol{\nabla}[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')\right.\right.\right.\\
& \left.\left.+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]d\mathbf{x}'\,d\mathbf{x}''\right\rangle\right\rangle\\
& -\left\langle\left\langle\int_{\Omega^2}\boldsymbol{\nabla}\,(\ln f\,)[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')\right.\right.\\
& \left.\left.\left.+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')H(\mathbf{m},\mathbf{x}-\mathbf{x}')]d\mathbf{x}'\,d\mathbf{x}''\right\rangle\right\rangle\right]\\
= & -\frac{kT}{4}\left\langle\left\langle\int_{\Omega^2}f(\mathbf{m},\mathbf{x},t)\boldsymbol{\nabla}\left[\frac{1}{f}[B(\mathbf{m},\mathbf{m}',\mathbf{x}'-\mathbf{x})\right.\right.\right.\\
& \times H(\mathbf{m}',\mathbf{x}''-\mathbf{x}')+B(\mathbf{m}',\mathbf{m},\mathbf{x}'-\mathbf{x}'')\\
& \left.\left.\left.\times H(\mathbf{m},\mathbf{x}-\mathbf{x}')]\right]d\mathbf{x}'\,d\mathbf{x}''\right\rangle\right\rangle.
\end{aligned}
\tag{A10}
$$

In the derivation, we notice that the existence of the extra elastic body force is related to the kernel function *BH*, which is the source of the nonlocal (long-range) molecular interaction.

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[1] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, United Kingdom, 1986).

[2] M. Doi, T. Shimada, and K. Okano, J. Chem. Phys. **88**, 4070 (1988).

[3] T. Shimada, M. Doi, and K. Okano, J. Chem. Phys. **88**, 7181 (1988).

[4] G. Marrucci and F. Greco, Mol. Cryst. **206**, 17 (1991).

[5] A. V. Bhave, Ph.D. thesis, MIT, 1992.

[6] J. Feng, G. Scalary, and G. Leal, J. Rheol. **44**, 1085 (2000).

[7] Q. Wang, J. Chem. Phys. (to be published).

[8] B. Bird, R. Armstrong and O. Hassager, *Dynamics of Polymeric Liquids V.1-2* (Wiley, New York, 1987).

[9] C. Murotov and W. E., J. Chem. Phys. **116**, 4723 (2002).

[10] P. G. DeGennes and Prost, *The Physics of Liquid Crystals* (Oxford University Press, United Kingdom, 1993).

[11] V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer-Verlag, New York, 1989).