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WEAKLY NONLINEAR VISCOELASTIC NEMATODYNAMICS

A. I. Leonov[a] **and V. S. Volkov**[b]

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A weakly nonlinear viscoelastic theory is developed for nematic liquid crystalline (LC) polymers. A small transient elastic strain due to the change in length of macromolecular strands under stress and a director of unit length are employed in the theory as hidden variables. The theory allows describing anisotropic viscoelasticity and the evolution equation for the director in flows of relatively rigid LC polymers or in slow flows of LC polymers with flexible spacers. As shown, omitting the director gradient does not affect macroscopic predictions of the theory. In the infinitesimal case, the evolution equation for the director looks like the Ericksen equation, but with an additional relaxation term. Although the present theory is mostly applicable for thermotropic LC polymers it can also be used for concentrated lyotropic LC systems, as well as for analyzing flows of concentrated polymer suspensions and nano-composites filled with uniaxially symmetric particles.

1. Introduction. Polymer liquid crystals consisting of relatively rigid macromolecules belong to a class of anisotropic polymer materials that combine the properties of liquid crystals and liquid or solid polymers [1]. There are two basic types of LC polymeric fluids: (i) lyotropic and thermotropic polymers consisting of fairly rigid monomer units, which are only commercially available, and (ii) the LC polymers with flexible spacers where the rigid monomer units belong either to the backbone or to side chains. There is also a class of solid LC elastomers where the LC macromolecules in elastomers of the second type are crosslinked. In contrast to common polymeric fluids, LC polymers exhibit during flow anisotropic viscoelastic properties characterized by both anisotropic relaxation times and viscosities. The solid-like LC elastomers also exhibit nonlinear, anisotropic, mechanical and other properties in thermodynamic equilibrium, in addition to nonlinear anisotropic relaxations characteristic of LC polymer fluids.

Numerous theoretical efforts were made to develop molecular theories that could model the lyotropic LC polymers. These highly publicized [2–6], mainstream theories typically use the Doi molecular, long rigid-rod approach [2, 3] with further elaborations. The Poisson–Bracket (PB) continuum theory has also been developed for deriving constitutive equations for LC polymers [7, 8]. It reduces to the Doi theory in the monodomain limit. Note that Dzyaloshinskii and Volovick [9] were the first to develop the PB nonlinear dynamics for low-molecular-weight (LMW) liquid crystals. There have also been some unsuccessful attempts to utilize the Leslie–Ericksen theory [10], elaborated for LMW liquid crystals to describe flows of thermotropic LC polymers.

All the above theories [2–8, 10] employ the same state variables for LC polymers as in the case of LMW liquid crystals, i.e., the director **n** (or the second-rank order tensor) and the director's space gradient, $\nabla \otimes \mathbf{n}$. Surprisingly, none of these theories is capable of describing the viscoelastic experimental data for LC polymers. For example, in the mono-domain limit these theories incorrectly predict that the dynamic modulus vanishes when the director is parallel either to the flow or to the flow gradient direction (see, e.g., [11]).

It is well known that for LMW liquid crystals the common solid-like elasticity is insignificant and the rotation mobility of small molecules, idealized as rigid rods, dominates. On the contrary, in high-molecular-weight polymeric liquid crystals with a typical degree of polymerization of several hundreds, the new quality due to the nature of long-chain molecules comes into action. This is the flexibility of long molecular chains, even with highly rigid monomer units, not mentioning the LC polymer with flexible spacers and LC elastomers. The molecular nature of this flexibility might be different for the above two types of LC polymers.

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[a]The University of Akron, Akron, Ohio 44325-0301, USA; email: leonov@uakron.edu; [b]Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Ave., Moscow, 117912, Russia; email: vsvolk@ips.ac.ru. Published in Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 3, pp. 31–38, May–June, 2003. Original article submitted November 12, 2002.

A good example of where the molecular flexibility plays a dominant role is the equilibrium behavior of LC elastomers. De Gennes [12] first used continuum thermodynamics to analyze weak nematic elasticity, involving the director gradient in the set of state variables. Later, Warner (e.g., see the recent publication [13] and the references therein) extended the De Gennes approach for finite deformations and finite rotations of LC elastomers, ignoring the director gradient. The statistical theory of rubber elasticity was also extended in these papers to the case of nematic-type anisotropy.

Attempts to include in the theory the molecular flexibility of LC polymers of both types were first discussed in the original Russian versions of the papers, which were later published in English [14–16]. This approach was aimed at studying anisotropic viscoelasticity of monodisperse LC polymers in slow relaxation regions. A continuum theory of anisotropic viscoelasticity of LC semi-flexible polymers was initiated in those papers, however, without thermodynamic analysis. The theory [14–16] extended the Maxwell constitutive equation to the anisotropic case, with uniaxial symmetry and small transient elastic strains. The field-induced orientation of the director described in several papers [14–16] demonstrated that the highest deviation from isotropic behavior occurs when the director is oriented along the velocity gradient. This result is consistent with the data obtained by Porter and Johnson [17].

Pleiner and Brand [18, 19] were the first to develop a linear non-equilibrium thermodynamic scheme, however, not in a minimal sense: in their description of LC polymers with flexible spacers, they took into account the space gradients of thermodynamics state variables. Rey [20, 21] also applied the irreversible thermodynamics approach for describing nonlinear phenomena in flow of LC polymers with flexible spacers. He employed as the state variables the director and small transient elastic strains. However, his free energy expression consisted of very specific terms of doubtful significance. His approach also contains several fundamental errors, e.g., the occurrence of an asymmetrical stress component in his thermodynamic scheme, and also incorrectly predicts vanishing of the dynamic modulus when the director is parallel either to the flow or to the flow gradient direction [21].

At present, polymer "nematodynamics," i.e., a thermodynamically related continuum theory of viscoelasticity for LC polymers, is still significantly undeveloped. The recent attempt [22] to develop a molecular insight into polymer nematodynamics did not produce a descriptive set of anisotropic viscoelastic constitutive relations, even in the linear case. It should also be noted that while a comprehensive microscopic theory of low-molecular-weight LC's currently does not exist, the dynamic properties of these LC's have been successfully described by nematodynamic theories.

Although a completely nonlinear approach has been sketched in [23], it is still too general to use it in describing experiments. Therefore, the present paper develops thermodynamically related, weakly nonlinear constitutive equations, which describe the viscoelastic and orientation properties of polymer nematics. Our theory may also be applied for flow analyses of concentrated suspensions with axially symmetric particles suspended in polymer fluids.

2. Thermodynamic State Variables and Free-Energy Function. To develop a continuum theory of nematic LC polymers, we introduce along with temperature T two thermodynamic hidden variables. The first one, the director, is a unit vector $\mathbf{n}$ that characterizes the physical properties of uniaxial anisotropy in LC polymers. The relation of the director to the microscopic characteristics of liquid crystals has been discussed in [24]. Another hidden variable in the theory is a symmetric second-rank tensor $\boldsymbol{\varepsilon}$ of a small norm ($|\boldsymbol{\varepsilon}| << 1$) that characterizes the elastic deformations in polymeric fluids. It is defined in a common way via the finite transient elastic strain tensor $\mathbf{c}$ as $\boldsymbol{\varepsilon} = 1/2\,(\mathbf{c} - \boldsymbol{\delta})$. The tensor $\mathbf{c}$ is, in turn, related to the "conformation tensor," the average dyadic $\langle \mathbf{R} \otimes \mathbf{R} \rangle$ built up on the end-to-end vector $\mathbf{R}$ between the ends of macromolecular strands and normalized with its equilibrium value. The elastic tensor $\boldsymbol{\varepsilon}$ turns out to be of a small norm when the characteristic relaxation time of the system is small enough. In this case, one can expect that the Weissenberg number of the system, We = $U\theta/L$, is also very small, even if the rates of deformation are high enough. Here θ, U, and L represent, respectively, the characteristic relaxation time, velocity, and length scale of the flow.

Neglecting the effect of the director gradient can be, e.g., justified for LC polymers when using the rubber elasticity concept. Comparing a typical gradient term in Frank energy density [10] (Sec. 3) with the rubber elastic term, one can conclude that omitting the director gradient term is validated in the length scale more than $\sqrt{k/\mu} \sim 10$ nm.

When the external (electrical or magnetic) fields are absent and the effects of the director gradient and inertia of internal rotations are ignored, the stress tensor is proven to be symmetric and the full energy of the system per mass unit is the sum of the kinetic and internal energies. Being interested mostly in isothermal situations, we can introduce, instead of the internal energy, the Helmholtz free energy f per mass unit, $f = f(T, \mathbf{n}, \boldsymbol{\varepsilon})$, which should be invariant relative to the transformation $\mathbf{n} \to -\mathbf{n}$. Additionally, we use the simplifying incompressibility assumption, common for polymeric liquids. Then the free energy of the system vanishing in the equilibrium ($\boldsymbol{\varepsilon} \to \mathbf{0}, \mathbf{n} \to \mathbf{n}_0$) is represented with an accuracy of $O(\boldsymbol{\varepsilon}^2)$ as a positive-definite, quadratic-linear form of tensor $\boldsymbol{\varepsilon}$ and director $\mathbf{n}$:

$$\rho f = 1/2\, G_0 \,\mathrm{tr}\,(\boldsymbol{\varepsilon}^2) + G_1 \,\mathrm{tr}\,(\mathbf{n} \otimes \mathbf{n}\cdot\boldsymbol{\varepsilon}^2) + G_1^1 \,[\mathrm{tr}\,(\mathbf{n} \otimes \mathbf{n}\cdot\boldsymbol{\varepsilon})]^2 + 1/2\, G_2 \,\mathrm{tr}\,(\mathbf{n} \otimes \mathbf{n}\cdot\boldsymbol{\varepsilon})\,. \tag{1}$$

Here G_0, G_1, G_1^1, and G_2 are temperature-dependent shear "moduli" in the model. The last term in (1) describes the possible yield in the system, with non-vanishing stress at the equilibrium. To simplify Eq. (1), we consider a special mobile coordinate system where the director takes the form $\mathbf{n} = \hat{\mathbf{n}} = \{1, 0, 0\}$ and $\boldsymbol{\varepsilon} = \hat{\boldsymbol{\varepsilon}}$. Then Eq. (1) takes the form

$$\rho f = 1/2\, G_0 \,\mathrm{tr}\,(\hat{\varepsilon}^2) + G_1 \,\mathrm{tr}\,(\hat{\varepsilon}_{11}^2 + \hat{\varepsilon}_{12}^2 + \hat{\varepsilon}_{13}^2) + G_1^1 \hat{\varepsilon}_{11}^2 + 1/2\, G_2 \hat{\varepsilon}_{11}\,.$$

Here the minimum value of the free energy, whose quadratic terms still hold convexity at any strain tensor $\hat{\boldsymbol{\varepsilon}}$, is achieved when $G_1^1 = -G_1$, the values of moduli G_0 and G_1 being positive. Thus, the minimized free-energy function has the final form

$$\rho f = 1/2\, G_0 \,\mathrm{tr}\,(\boldsymbol{\varepsilon}^2) + G_1 \left\{\mathrm{tr}\,(\mathbf{n} \otimes \mathbf{n}\cdot\boldsymbol{\varepsilon}^2) - [\mathrm{tr}\,(\mathbf{n} \otimes \mathbf{n}\cdot\boldsymbol{\varepsilon})]^2\right\} + 1/2\, G_2 \,\mathrm{tr}\,(\mathbf{n} \otimes \mathbf{n}\cdot\boldsymbol{\varepsilon})\,. \tag{2}$$

As seen from the above derivation of Eq. (2), the second term on its right-hand side is positive, whereas the last term on the right-hand side represents the anisotropic yield with the sign-indefinite "modulus" G_2.

It should be mentioned that expression (2) is different from those [12, 13] used in the equilibrium, solid-like nematic elasticity. First, we neglected the director gradient term, contained in [12], and more importantly, Eq. (2) does not contain the relative rotations [12, 13] $\boldsymbol{\Omega}_{\mathrm{r}} = \boldsymbol{\Omega} - \boldsymbol{\Omega}_{\mathrm{i}}$, where $\boldsymbol{\Omega}$ and $\boldsymbol{\Omega}_{\mathrm{i}}$ are, respectively, the body and internal rotation tensors. To justify the above approach, we now outline the "renormalization" procedure of derivation of Eq. (2) (without the yield term) from the general expressions in [12, 13] demonstrated in the case of small elastic strains in [29]. Starting from the general expression for free energy, containing $\boldsymbol{\Omega}_{\mathrm{r}}$, it is easy to calculate the asymmetric part of the stress tensor $\boldsymbol{\sigma}_{\mathrm{a}}$. When the external (magnetic or electrical) fields are absent and the internal inertia effects are negligible, the stress tensor is symmetric (e.g., see [29]), i.e., $\boldsymbol{\sigma}_{\mathrm{a}} = \mathbf{0}$. This equality serves as an additional relation for expressing $\boldsymbol{\Omega}_{\mathrm{r}}$ via $\boldsymbol{\varepsilon}$ and $\mathbf{n}$. Substituting $\boldsymbol{\Omega}_{\mathrm{r}}$ into the initial expressions for both the free-energy function and the symmetric part of the stress tensor results in Eq. (2) as a renormalized equation, with renormalized initial thermodynamic constraints and a potential relation between free energy and stress.

3. Entropy Production and Thermodynamic Fluxes and Forces. We adopt below all the basic assumptions of the non-equilibrium thermodynamics [25, 26], such as "closeness" to the equilibrium and the local equilibrium assumption. Utilizing the laws of mass, energy, and momentum conservation and using the routine derivation procedure [25, 26], one can obtain the frame-invariant expression for the dissipation D (or the entropy production P_{s} under isothermal conditions) in the system as follows:

$$D \equiv TP_{\mathrm{s}}\,\big|_T = \mathrm{tr}\,(\boldsymbol{\sigma}\cdot\mathbf{e}) - \rho\dot{f}\,\big|_T = \mathrm{tr}\,(\boldsymbol{\sigma}\cdot\mathbf{e}) - \rho\,\mathrm{tr}\,(\partial f/\partial\boldsymbol{\varepsilon}\cdot\overset{0}{\boldsymbol{\varepsilon}}) + \rho\partial\tilde{f}/\partial\mathbf{n}\cdot\overset{0}{\mathbf{n}} \quad (\geq 0)\,. \tag{3}$$

The symbol ≥ in (3) means that the dissipation is positive for all irreversible processes and vanishes in the thermodynamic equilibrium. In Eq. (3), ρ is the density, $\boldsymbol{\sigma}$ is the traceless, symmetric extra-stress tensor (stress tensor minus isotropic pressure term), and $\mathbf{e} = 1/2\,[\nabla \otimes \mathbf{u} + (\nabla \otimes \mathbf{u})^T]$ is the traceless, symmetric strain-rate tensor, where $\mathbf{u}$ is the velocity vector. In Eq. (3), $\overset{0}{\boldsymbol{\varepsilon}} = \dot{\boldsymbol{\varepsilon}} - \boldsymbol{\varepsilon}\cdot\boldsymbol{\omega} + \boldsymbol{\omega}\cdot\boldsymbol{\varepsilon}$ and $\overset{0}{\mathbf{n}} = \dot{\mathbf{n}} - \mathbf{n}\cdot\boldsymbol{\omega}$ are the co-rotational (Jaumann) time derivatives. Here $\boldsymbol{\omega} = 1/2\,[\nabla \otimes \mathbf{u} - (\nabla \otimes \mathbf{u})^T]$ is the anti-symmetric vorticity tensor and overdots mean the material time derivatives. To hold the constraint $|\mathbf{n}| = 1$ during the differentiation, one should introduce the scalar Lagrange multiplier q and modify the free energy f for $\tilde{f}$ as follows: $\tilde{f} = f(T, \mathbf{n}, \boldsymbol{\varepsilon}) - 1/2\, q\mathbf{n}\cdot\mathbf{n}$. The same holds for the pressure p included in the full stress tensor.

It is seen that the dissipation in (3) is represented as a bilinear form, $D = \sum_k X_k Y_k$, where the thermodynamic forces X_k are chosen to characterize dynamic variables and the thermodynamic fluxes Y_k conjugated to them represent the kinematic variables. For example, the stress and strain-rate tensors $\boldsymbol{\sigma}$ and $\mathbf{e}$ represent the external conjugated thermodynamic force and flux, respectively.

The completely nonlinear situation, determining the thermodynamic forces and fluxes related to the hidden variables, is generally not a trivial problem [23]. However, in our weakly nonlinear case, these variables are defined relatively easily. The thermodynamic flux and thermodynamic force related to the director conjugated to it are respectively the vectors $\overset{0}{\mathbf{n}}$ and $\rho\partial f/\partial\mathbf{n}$. As the thermodynamic flux and the thermodynamic force conjugated to it, related to $\boldsymbol{\varepsilon}$, we accept the tensors $\overset{0}{\boldsymbol{\varepsilon}}$ and $\rho\partial f/\partial\boldsymbol{\varepsilon}$. Accepting $\overset{0}{\boldsymbol{\varepsilon}}$ as the thermodynamic flux has an approximate, modeling character [23]. Nevertheless, this approximation leads to a good prediction of anisotropic viscoelastic effects when We << 1. Thus, the above thermodynamic forces with an accuracy of $O(\boldsymbol{\varepsilon})$ have the form

$$\mathbf{N} \equiv -\rho\partial f/\partial\mathbf{n} \approx -G_2\,\boldsymbol{\varepsilon}\cdot\mathbf{n}\,; \tag{4a}$$

$$\boldsymbol{\sigma}_\mathrm{e} \equiv \rho\partial f/\partial\boldsymbol{\varepsilon} = G_0\boldsymbol{\varepsilon} + G_1\,[\mathbf{n}\otimes\mathbf{n}\cdot\boldsymbol{\varepsilon} + \boldsymbol{\varepsilon}\cdot\mathbf{n}\otimes\mathbf{n} - 2\mathbf{n}\otimes\mathbf{n}\cdot\mathrm{tr}\,(\mathbf{n}\otimes\mathbf{n}\cdot\boldsymbol{\varepsilon})] + G_2\,(\mathbf{n}\otimes\mathbf{n} - 1/3\,\boldsymbol{\delta})\,. \tag{4b}$$

Substituting (4) into (3) yields

$$D = TP_\mathrm{s}\,\big|_T = \mathrm{tr}\,(\boldsymbol{\sigma}\cdot\mathbf{e}) - \mathrm{tr}\,(\boldsymbol{\sigma}_\mathrm{e}\cdot\mathbf{e}_\mathrm{e}) + \mathbf{N}\cdot\overset{0}{\mathbf{n}}\,. \tag{5}$$

Because the director $\mathbf{n}$ has unit length, the "orientation" force $\mathbf{N}$ can be replaced without loss of generality by $\tilde{\mathbf{N}} = \mathbf{N} - q\mathbf{n}$. Here q is the Lagrange multiplier defined in (3) to hold the constraint $\mathbf{n}\cdot\mathbf{n} = 1$, and, correspondingly, $\mathbf{n}\cdot\dot{\mathbf{n}} = \mathbf{n}\cdot\overset{0}{\mathbf{n}} = 0$.

Conjugated thermodynamic force and flux, tensors $\boldsymbol{\sigma}_\mathrm{e}$ and $\overset{0}{\boldsymbol{\varepsilon}}$, have natural limits in the anisotropic solid equilibrium. Therefore it is convenient to introduce, as has been done for isotropic viscoelasticity [27, 28], the non-equilibrium thermodynamic force $\boldsymbol{\sigma}_\mathrm{p}$ and flux $\mathbf{e}_\mathrm{p}$ that vanish in equilibrium:

$$\boldsymbol{\sigma}_\mathrm{p} = \boldsymbol{\sigma} - \boldsymbol{\sigma}_\mathrm{e}\,;\quad \mathbf{e}_\mathrm{p} = \mathbf{e} - \overset{0}{\boldsymbol{\varepsilon}}\,. \tag{6}$$

Because the right-hand side in the second relation (6) is traceless, $\mathrm{tr}\,\mathbf{e}_\mathrm{p} = 0$. Note that the tensors $\boldsymbol{\sigma}_\mathrm{p}$ and $\mathbf{e}_\mathrm{p}$ in (6) have yet to be determined from the set of constitutive equations.

Substituting (6) into (5) yields the most convenient form for dissipation:

$$D = TP_\mathrm{s}\,\big|_T = \mathrm{tr}\,(\boldsymbol{\sigma}_\mathrm{p}\cdot\mathbf{e}) + \mathrm{tr}\,(\boldsymbol{\sigma}_\mathrm{e}\cdot\mathbf{e}_\mathrm{p}) + \mathbf{N}\cdot\overset{0}{\mathbf{n}} \quad (\geq 0)\,. \tag{7}$$

Equation (7) clearly shows the three sources of dissipation: (i) deviation of the stress tensor from the thermodynamic one ($\boldsymbol{\sigma}_\mathrm{p} \equiv \boldsymbol{\sigma} - \boldsymbol{\sigma}_\mathrm{e} \neq \mathbf{0}$), (ii) deviation of the strain-rate tensor from the thermodynamic one ($\mathbf{e}_\mathrm{p} \equiv \mathbf{e} - \mathbf{e}_\mathrm{e} \neq \mathbf{0}$), and (iii) the presence of the orientation force ($N \neq 0$).

4. Constitutive Relations. In the present weakly nonlinear theory, the constitutive relations between thermodynamic forces and fluxes are quasi-linear, i.e., they are linear but the phenomenological coefficients are considered as functions of director **n**. Onsager’s symmetry of phenomenological coefficients has been proven for both the linear [25, 26] and quasi-linear [30] cases. The positiveness of dissipation imposes some additional constraints on the phenomenological coefficients. In accordance with Eq. (7), the thermodynamic forces are defined as $\boldsymbol{\sigma}_\mathrm{p}$, $\tilde{\boldsymbol{\sigma}}_\mathrm{e}$, and $\mathbf{N}$. Here $\tilde{\boldsymbol{\sigma}}_\mathrm{e} \equiv \boldsymbol{\sigma}_\mathrm{e} - G_2(\mathbf{n}\otimes\mathbf{n} - 1/3\,\boldsymbol{\delta})$ is introduced instead of $\boldsymbol{\sigma}_\mathrm{e}$. This is because, in contrast to plasticity theories, the "yield" term $G_2(\mathbf{n}\otimes\mathbf{n} - 1/3\,\boldsymbol{\delta})$ has an equilibrium, non-dissipative character. The thermodynamic fluxes conjugated to these thermodynamic forces, respectively, are $\mathbf{e}$, $\mathbf{e}_\mathrm{p}$, and $\overset{0}{\mathbf{n}}$. The quasi-linear phenomenological relations between the thermodynamic fluxes and forces with account for Onsager symmetry are

$$e_{ij} = A^{(11)}_{ijkl}\ \sigma^{\mathrm{p}}_{lk} + A^{(12)}_{ijkl}\ \tilde{\sigma}^{\mathrm{e}}_{lk} + b^{(13)}_{ij,k}\ N_k\ ; \tag{8.1}$$

$$e^{\mathrm{p}}_{ij} = A^{(12)}_{ijkl}\ \sigma^{\mathrm{p}}_{lk} + A^{(22)}_{ijkl}\ \tilde{\sigma}^{\mathrm{e}}_{lk} + b^{(23)}_{ij,k}\ N_k\ ; \tag{8.2}$$

$$\overset{\circ}{n}_k = b^{(13)}_{ij,k}\ \sigma^{\mathrm{p}}_{ji} + b^{(23)}_{ij,k}\ \tilde{\sigma}^{\mathrm{e}}_{ji} + a_{ki}\ N_i\ . \tag{8.3}$$

Here all the kinetic coefficients, tensors of various rank in (8), are some functions of temperature T and vector $\mathbf{n}$. The fourth-rank kinetic tensors $A^{(st)}_{ijkl}$ $(s, t = 1, 2)$ are symmetric and traceless in the first two and the second two pairs of indices and in transposition of the first and second pairs of indices. The third-rank kinetic tensors $b^{(s3)}_{ij,k}$ $(s = 1, 2)$ are symmetric and traceless in the first pair of indices. Because $|\mathbf{n}| = 1$, there is the evident constraint $b^{(s3)}_{ij,k} n_k = 0$. The second-rank kinetic tensor $\mathbf{a}$ is symmetric and also has the following constraint: $a_{ki} n_k = 0$.

The structures of these tensors are represented as follows:

$$A^{(st)}_{ijkl}\,(\mathbf{n}) = (1/\eta^{st}_0)\ \alpha^{(1)}_{ijkl} + (1/\eta^{st}_1)\ \alpha^{(2)}_{ijkl}\,(\mathbf{n})\ ;\quad \alpha^{(1)}_{ijkl} = 1/2\ (\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il} - 2/3\ \delta_{ij}\delta_{kl})\ ;$$

$$\alpha^{(2)}_{ijkl}\,(\mathbf{n}) = 1/2\ (\delta^{\perp}_{ik} n_l n_j + \delta^{\perp}_{jk} n_l n_i + \delta^{\perp}_{il}\, n_k n_j + \delta^{\perp}_{jl}\, n_k n_i)\ ; \tag{9}$$

$$a_{ik} = (1/\eta_2)\ \delta^{\perp}_{ik}\ ;\quad \delta^{\perp}_{ij} = \delta_{ij} - n_i n_j\ ; \tag{10}$$

$$b^{s3}_{ij,k} = (1/\eta^{s3}_3)\ \beta_{ij,k}\,(\mathbf{n})\ ;\quad \beta_{ij,k}\,(\mathbf{n}) = \delta^{\perp}_{ik} n_j + \delta^{\perp}_{jk} n_i\ . \tag{11}$$

Here $\delta^{\perp}_{ij}$ is the transverse Kronecker symbol, which makes a projection on the direction orthogonal to the director; η^{st}_k are temperature-dependent "viscosities." The properties of numerical tensors $\alpha^{(1,2)}_{ijkl}(\mathbf{n})$ and $\beta_{ij,k}(\mathbf{n})$ are considered in the Appendix.

Substituting (8) into (7) yields the expression for dissipation presented as a quadratic form of the thermodynamic forces:

$$D = TP_{\mathrm{s}}\big|_T = A^{(11)}_{ijkl}\sigma^{\mathrm{p}}_{ij}\sigma^{\mathrm{p}}_{lk} + 2A^{(12)}_{ijkl}\sigma^{\mathrm{p}}_{lij}\sigma^{\mathrm{e}}_{lk} + A^{(22)}_{ijkl}\sigma^{\mathrm{e}}_{ij}\sigma^{\mathrm{e}}_{lk} + 2b^{(13)}_{ij,k}\sigma^{\mathrm{p}}_{ij}N_k + 2b^{(23)}_{ij,k}\sigma^{\mathrm{e}}_{ij}N_k + a_{ik}N_iN_k\ . \tag{12}$$

The positive-definiteness of dissipation D imposes additional constraints on the kinetic tensors, e.g., the fourth-rank tensors $\mathbf{A}^{(11)}$ and $\mathbf{A}^{(22)}$ and the second-rank tensor $\mathbf{a}$ should be positive-definite. Also, some additional constraints should be imposed on the combination of these tensors. All these constraints guarantee the existence of inverse constitutive relations, which represent the "dual" quasi-linear relations between the thermodynamic forces $\boldsymbol{\sigma}_{\mathrm{p}}$, $\boldsymbol{\sigma}_{\mathrm{e}}$, and $\mathbf{N}$ and the thermodynamic fluxes $\mathbf{e}$, $\mathbf{e}_{\mathrm{p}}$, and $\overset{0}{\mathbf{n}}$, with the dual kinetic coefficients having the same structure as in Eqs. (9)–(11).

The second relation in (6) presents the evolution equation for the thermodynamic parameter $\boldsymbol{\varepsilon}$, as soon as the irreversible strain-rate tensor $\mathbf{e}_{\mathrm{p}}$ is expressed via other thermodynamic forces, as shown in (8). The evolution equation for the director $\mathbf{n}$ is presented as the third equation in (8). Equations (6) and (8)–(11), along with definitions (4) for $\mathbf{N}$ and $\boldsymbol{\sigma}_{\mathrm{e}}$, represent a closed set of anisotropic viscoelastic constitutive equations for LC polymeric liquids. There are also three important particular (limit) cases:

(i) *Anisotropic solid-like behavior of the Kelvin–Voight type.* This occurs when the irreversible strain rate $\mathbf{e}_{\mathrm{p}}$ in (6) and (8) vanishes. In this case the elastic strain $\boldsymbol{\varepsilon}$ is equal to the total one. There are two sources of irreversibility there: the difference between the actual stress $\boldsymbol{\sigma}$ and thermodynamic (equilibrium) stress $\boldsymbol{\sigma}_{\mathrm{e}}$ ($\boldsymbol{\sigma}_{\mathrm{p}} \neq \mathbf{0}$) and the evolution of the director ($\mathbf{N} \neq \mathbf{0}$). The constitutive equations here present a limiting case of (8), where

$$\mathbf{A}^{(12)} = \mathbf{A}^{(22)} = \mathbf{0}\ ;\quad \mathbf{b}^{(23)} = \mathbf{0}\ . \tag{13}$$

(ii) *Anisotropic liquid-like viscous behavior of Ericksen type.* This occurs when $\mathbf{e}_\mathrm{p} = \mathbf{e}$, meaning that $\boldsymbol{\varepsilon} = \mathbf{0}$. Therefore, $\mathbf{N} = \mathbf{0}$ and $\boldsymbol{\sigma}_\mathrm{e} = \mathbf{0}$. In this case $\mathbf{b}^{(13)} \neq \mathbf{0}$ and the irreversibility comes from the terms proportional to $\mathbf{A}^{(11)} = \mathbf{A}^{(12)} \neq \mathbf{0}$. Using Eqs. (9), (11), and the formulas in the Appendix, we easily reduce Eqs. (8) to the Ericksen one (e.g., [10]).

(iii) *The liquid-like behavior of the Maxwell type* is described in the next section.

5. Constitutive Equations for Weakly Nonlinear Maxwell Anisotropic Liquids. The Maxwell case occurs when the irreversible stress $\boldsymbol{\sigma}_\mathrm{p} = \mathbf{0}$ in (6). This means that, in this case, the thermodynamic extra-stress $\boldsymbol{\sigma}_\mathrm{e}$ defined in (4) coincides with the actual extra-stress $\boldsymbol{\sigma}$. The irreversibility here comes from the existence of irreversible deformations ($\mathbf{e}_\mathrm{p} \neq \mathbf{0}$) and the evolution of the director ($\tilde{\mathbf{N}} \neq \mathbf{0}$). The constitutive equations are described by a limit case of (8), where

$$\mathbf{A}^{(11)} \to \infty\, ; \quad \mathbf{A}^{(12)} = \mathbf{0}\, ; \quad \mathbf{b}^{(13)} = \mathbf{0}\, . \tag{14}$$

The free energy of the system is represented in Eq. (2), with orientation force $\mathbf{N}$ and extra-stress tensor $\boldsymbol{\sigma} = \boldsymbol{\sigma}_\mathrm{e}$ being defined in Eq. (4), with the evolution equation for tensor $\boldsymbol{\varepsilon}$ being presented in the second relation in (6). The phenomenological relations (8) with account of (9)–(11) are simplified with the use of (14). Using the properties of numerical tensors $\boldsymbol{\alpha}^{(1,2)}(\mathbf{n})$ and $\boldsymbol{\beta}(\mathbf{n})$ proved in the Appendix, we write the closed set of constitutive equations as follows:

$$\overset{0}{\boldsymbol{\varepsilon}} + (1/\theta_0)\, \boldsymbol{\varepsilon} + (1/\theta_1)\, [\mathbf{n} \otimes \mathbf{n}{\cdot}\boldsymbol{\varepsilon} + \boldsymbol{\varepsilon}{\cdot}\mathbf{n} \otimes \mathbf{n} - 2\mathbf{n} \otimes \mathbf{n}\, \mathrm{tr}\, (\mathbf{n} \otimes \mathbf{n}{\cdot}\boldsymbol{\varepsilon})] = \mathbf{e}\, ; \tag{15}$$

$$\overset{0}{\mathbf{n}} = (1/\theta_2)\, [\boldsymbol{\varepsilon}{\cdot}\mathbf{n} \; - \mathbf{n}\, \mathrm{tr}\, (\boldsymbol{\varepsilon}{\cdot}\mathbf{n} \otimes \mathbf{n})]\, ; \tag{16}$$

$$\boldsymbol{\sigma}_\mathrm{e} \equiv \rho \partial f/\partial \boldsymbol{\varepsilon} = G_0 \boldsymbol{\varepsilon} + G_1\, [\mathbf{n} \otimes \mathbf{n}{\cdot}\boldsymbol{\varepsilon} + \boldsymbol{\varepsilon}{\cdot}\mathbf{n} \otimes \mathbf{n} - 2\mathbf{n} \otimes \mathbf{n}{\cdot}\mathrm{tr}\, (\mathbf{n} \otimes \mathbf{n}{\cdot}\boldsymbol{\varepsilon})] + G_2\, (\mathbf{n} \otimes \mathbf{n} - 1/3\, \boldsymbol{\delta})\, . \tag{17}$$

Here θ_0, θ_1, and θ_2 are the relaxation times in the model, θ_0 and θ_1 being positive and θ_2 sign-indefinite. They are represented via the parameters G_k and η_k as

$$\theta_0 = \frac{\eta_0}{G_0}\, ; \quad \theta_1 = \left(\frac{G_1}{\eta_0} + \frac{G_0 + G_1}{\eta_1} + \frac{G_2}{\eta_2} \right)^{-1}\, ; \quad \theta_2 = \left(\frac{G_0 + G_1}{\eta_3} + \frac{G_2}{\eta_2} \right)^{-1}\, . \tag{18}$$

Here, in the notation of Eqs. (9)–(11), the viscosities η_k are presented as follows: $\eta_0 = \eta_0^{22}$; $\eta_1 = \eta_1^{22}$; $\eta_3 = \eta_3^{23}$. The general initial conditions for these equations are

$$\boldsymbol{\varepsilon}\,\big|_{t=0} = \boldsymbol{\varepsilon}_0\, , \quad \mathbf{n}\,\big|_{t=0} = \mathbf{n}_0\, . \tag{19}$$

We finally demonstrate that the constitutive equations proposed in [14–16] can be derived under certain conditions from equations derived in this section. Consider linearized equations for orientation, slightly different from those in equilibrium, when $\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n}$, with constitutive relations where the norm of the elastic strain $\boldsymbol{\varepsilon}$ is infinitesimal and the yield is ignored, i.e., $G_2 = 0$. Here $\mathbf{n}_0$ is the value of the director in equilibrium and $\delta\mathbf{n}$, being orthogonal to both $\mathbf{n}$ and $\mathbf{n}_0$, describes small rotations of the director relative to its initial state. Multiplying (16), where in the linear case $\overset{0}{\mathbf{n}} = \delta\dot{\mathbf{n}} - \mathbf{n}_0{\cdot}\boldsymbol{\omega}$, by the third-rank tensor $1/\eta_2\, \boldsymbol{\beta}(\mathbf{n}_0)$ and using Eqs. (A3) and (A4) from the Appendix yields with an accuracy of $O(\boldsymbol{\varepsilon})$ the linear equation for the director:

$$\tau \frac{d}{dt} \overset{0}{n}_k + \overset{0}{n}_k = \lambda\, (e_{kj} n_{0j} - n_{0k} n_{0i} n_{0j} e_{ij})\, ; \quad \tau = \frac{\eta_0 \eta_1}{(G_0 + G_1)\, (\eta_0 + \eta_1)}\, ; \quad \lambda = \frac{2\eta_0 \eta_1}{\eta_2\, (\eta_0 + \eta_1)}\, . \tag{20}$$

Here λ is a non-dimensional constant and τ is the orientation relaxation time. Equation (20) shows that the evolution equation for the director $\mathbf{n}$ reduces to the Ericksen equation, where the Weissenberg number defined with relaxation time τ should be considerably small, i.e., $\mathrm{We}_\tau = \tau U/L \ll 1$. The theory in this limit has been developed in [14]. Comparing that with other characteristic relaxation times that occur in (15), one can see a variety of asymptotic cases which can be found in flows. Using another approach, in [15] an orientation equation similar to Eq. (20) was derived, however in a less convenient form.

According to the evolution equation (20) for the director, the small disturbance $\delta\mathbf{n}$ is of the order of the velocity gradient. Using this fact along with the simplifications $\mathbf{N} = O(\boldsymbol{\varepsilon}^2) \approx \mathbf{0}$, $\mathrm{tr}\,\boldsymbol{\varepsilon} \approx 0$, and $\overset{0}{\boldsymbol{\varepsilon}} \approx \dot{\boldsymbol{\varepsilon}}$ that are evident in the linear case and the formulas in the Appendix, it is easy to represent Eqs. (15) and (17) as an anisotropic evolution (Maxwell-like) equation for the stress deviator:

$$\theta_{ijkl}\,(\mathbf{n}_0)\,\dot{\sigma}_{kl} + \sigma_{ij} \approx \eta_{ijkl}\,(\mathbf{n}_0)\,e_{kl}\,. \tag{21}$$

Here, using Eqs. (A5), (A6), and (A13) from the Appendix, we present the fourth-rank tensors of anisotropic viscosity and relaxations in the form

$$\eta = \eta_0\,[\alpha^{(1)} - r_2\alpha^{(2)}\,(\mathbf{n}_0)]\,; \quad \theta = (\eta_0/G_0)\,[\alpha^{(1)} - r_1\alpha^{(2)}\,(\mathbf{n}_0)]\,. \tag{22}$$

Here the numerical fourth-rank tensors $\alpha^{(1)}(\mathbf{n}_0)$ and $\alpha^{(2)}(\mathbf{n}_0)$ are defined in Eq. (9), and the non-dimensional coefficients r_1 and r_2 are

$$r_1 = \frac{(G_0 + G_1)/\eta_1 + G_1/\eta_0}{(G_0 + G_1)\,(1/\eta_1 + 1/\eta_0)}\,; \quad r_2 = \frac{\eta_0}{\eta_1 + \eta_0}\,. \tag{23}$$

The expression for dissipation (12) with account of (14) is

$$D = TP_{\mathrm{s}}\big|_T \approx A_{ijkl}\,(\mathbf{n})\,\sigma_{ij}\sigma_{lk} = 1/\eta_0\,\mathrm{tr}\,(\boldsymbol{\sigma}^2) + 1/\eta_1\left\{\mathrm{tr}\,(\mathbf{n}_0 \otimes \mathbf{n}_0\cdot\boldsymbol{\sigma}^2) - [\mathrm{tr}\,(\mathbf{n}_0 \otimes \mathbf{n}_0\cdot\boldsymbol{\sigma})]^2\right\}. \tag{24}$$

Equations (21) and (22) demonstrate that the linear viscoelasticity of nematic polymeric liquids near the rest state is completely determined by the initial orientation of the director.

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APPENDIX

Properties of Tensors Characterizing Uniaxial Anisotropy. The non-dimensional kinetic tensors $\alpha^{(1)}$, $\alpha^{(2)}$, and β, defined in Eqs. (9)–(11), possess the following multiplicative properties that can be checked by direct calculations:

$$\alpha^{(1)}_{ijmn}\,\alpha^{(2)}_{nmkl}\,(\mathbf{n}) = \alpha^{(2)}_{ijmn}\,(\mathbf{n})\,\alpha^{(1)}_{nmkl} = \alpha^{(2)}_{ijkl}\,(\mathbf{n})\,; \tag{A1}$$

$$\alpha^{(1)}_{ijmn}\,\alpha^{(1)}_{nmkl}\,(\mathbf{n}) = \alpha^{(1)}_{ijkl}\,(\mathbf{n})\,; \quad \alpha^{(2)}_{ijmn}\,\alpha^{(2)}_{nmkl}\,(\mathbf{n}) = \alpha^{(2)}_{ijkl}\,(\mathbf{n})\,; \tag{A2}$$

$$\beta_{ij,k}\alpha^{(1)}_{ijmn} = \beta_{mn,k}\,; \quad \beta_{ij,k}\alpha^{(2)}_{ijmn} = \beta_{mn,k}\,. \tag{A3}$$

We will also prove that a fourth-rank tensor,

$$\mathbf{S}\,(\mathbf{n}) = S_0\alpha^{(1)} + S_1\alpha^{(2)}\,(\mathbf{n})\,, \tag{A4}$$

is positive-definite when the constants S_0, $S_1 > 0$. We initially prove that the reciprocal tensor $\mathbf{S}^{-1}$ can be found from the equation

$$\mathbf{S}\,(\mathbf{n})\,\mathbf{S}^{-1}\,(\mathbf{n}) = \alpha^{(1)}\,. \tag{A5}$$

It is easy to prove that the general presentation for $\mathbf{S}^{-1}$ has the same form as shown in (A4), $\mathbf{S}^{-1}(\mathbf{n}) = \tilde{S}_0\alpha^{(1)} + \tilde{S}_0\alpha^{(2)}(\mathbf{n})$. Then unknown constants $\tilde{S}_0$ and $\tilde{S}_1$ are found by substituting this expression and (A5) into (A6). Thus, $\mathbf{S}^{-1}$ is presented in the form

$$\mathbf{S}^{-1}\,(\mathbf{n}) = \frac{1}{S_0}\left[\alpha^{(1)} - \frac{S_1}{S_0 + S_1}\,\alpha^{(2)}\,(\mathbf{n})\right]. \tag{A6}$$

The tensor $\mathbf{S}^{-1}$ in (A6) is positive-definite, because $\forall\mathbf{x} = \{x_{ij}\}$ $(\mathrm{tr}\,\mathbf{x} = 0,\ \mathbf{x} = \mathbf{x}^T)$:

$$S^{-1}_{ijkl}\,(\mathbf{n})\,x_{ij}x_{kl} = \frac{1}{S_0}\left[\mathrm{tr}\,(\mathbf{x}^2) - \frac{S_1}{S_0 + S_1}\left\{\mathrm{tr}\,(\mathbf{x}^2\cdot\mathbf{n}\otimes\mathbf{n}) - [\mathrm{tr}\,(\mathbf{x}\cdot\mathbf{n}\otimes\mathbf{n})]^2\right\}\right] \geq \frac{S_0\,\mathrm{tr}\,(\mathbf{x}^2) + S_1\,[\mathrm{tr}\,(\mathbf{x}\cdot\mathbf{n}\otimes\mathbf{n})]^2}{S_0\,(S_0 + S_1)} > 0\,.$$

Here the obvious inequality $\mathrm{tr}\,(\mathbf{x}^2\cdot\mathbf{n}\otimes\mathbf{n}) \leq \mathrm{tr}\,(\mathbf{x}^2)$ has been used. The above inequality also proves that the fourth-rank tensor $\mathbf{S}(\mathbf{n})$ in Eq. (A4) is positive-definite.

NOTATION

$A^{(st)}_{ijkl}$, a_{ij}, $b^{(st)}_{ij,k}$, kinetic coefficients; $\mathbf{c}$, finite transient elastic-strain tensor; D, dissipation; $\mathbf{e}$, strain-rate tensor; $\mathbf{e}_\mathrm{p}$, irreversible strain-rate tensor; f, Helmholtz elastic potential; $\tilde{f}$, modified elastic potential; G_0, G_1, G_2, elastic moduli; k, Frank elastic constant; L, characteristic flow length scale; $\mathbf{n}$, director; $\mathbf{n}_0$, value of the director in equilibrium; $\overset{0}{\mathbf{n}}$, Jaumann time derivative of the director; $\mathbf{N}$, orientation force; P_s, entropy production; q, Lagrange multiplier; $\mathbf{R}$, end-to-end vector; $\langle\mathbf{R}\otimes\mathbf{R}\rangle$, conformation tensor; r_1, r_2, non-dimensional constants; $\mathbf{S}$, fourth-rank tensor; S_0, S_1, non-dimensional constants; T, temperature; U, characteristic flow velocity; $\mathbf{u}$, velocity vector; We, Weissenberg number; $\mathbf{x}$, second-order, symmetric traceless tensor; X_k, Y_k, conjugated thermodynamic forces and fluxes; $\alpha^{(1,2)}$, $\boldsymbol{\beta}$, non-dimensional anisotropic tensors; $\boldsymbol{\varepsilon}$, small elastic transient strain tensor; $\overset{0}{\boldsymbol{\varepsilon}}$, Jaumann time derivative of $\boldsymbol{\varepsilon}$; $\dot{\boldsymbol{\varepsilon}}$, material time derivative of $\boldsymbol{\varepsilon}$; $\boldsymbol{\delta}$, unit tensor; $\delta^{\perp}_{ij}$, transverse Kronecker symbol; μ, rubber elasticity modulus; $\eta^{st}_0, \eta^{st}_1, \eta_2, \eta^{s3}_3$, scalar viscosities; $\boldsymbol{\eta}$, tensor of anisotropic viscosity; ∇, operator of space derivative; $\boldsymbol{\Omega}_\mathrm{r}$, $\boldsymbol{\Omega}_\mathrm{i}$, and $\boldsymbol{\Omega}$, tensors of relative, internal, and body rotation; ρ, density; $\boldsymbol{\sigma}_\mathrm{a}$, asymmetric part of stress tensor; $\boldsymbol{\sigma}$, complete (symmetric) extra-stress tensor; $\boldsymbol{\sigma}_\mathrm{e}$ and $\boldsymbol{\sigma}_\mathrm{p}$, elastic and inelastic parts of $\boldsymbol{\sigma}$; θ, characteristic relaxation time; θ_0, θ_1, θ_2, scalar relaxation times; $\boldsymbol{\theta}$, tensor of anisotropic relaxation.

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