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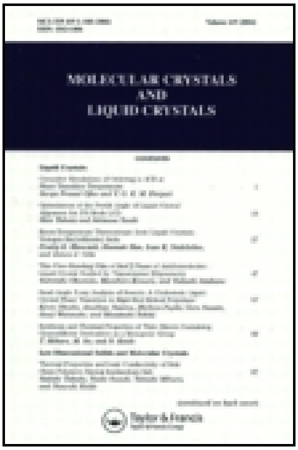

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Theory of Linear Viscoelasticity for Single-Phase Nematic Mixtures

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Theory of Linear Viscoelasticity for Single-Phase Nematic Mixtures

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A macroscopic model for incompressible homogeneous (single phase) binary nematic mixtures under isothermal conditions is given; the model is restricted to two miscible nematic liquid crystals. The rheological model is a generalization of the standard Ericksen's nematorheological model for single component uniaxial rod-like nematic liquid crystals. The theory is used to characterize the linear viscoelasticity of the nematic mixture when subjected to small amplitude oscillatory shear. Mixture elasticity is shown to predict a frequency dependence of the dynamic viscosity (η' and η'') essentially identical to those obtained using Frank elasticity and molecular elasticity. The composition dependence of the storage G' and loss modulus G'' is found to be nonlinear, and stronger at low frequency than at high frequency.

Keywords: Macroscopic theory, nematic mixtures, linear viscoelasticity, storage and loss moduli, dynamic viscosity.

1. INTRODUCTION

Improving product and processing properties through alloying and mixing is a commonly used route in industrial manufacturing.[1] Low molecular weight nematics used in display devices are routinely mixed to reduce the melting temperature, and many commercial nematic mixtures have the low-melting solid-nematic eutectic composition. Nematic polymers are also mixed and blended with the objective of reducing costs through viscosity reduction.[2] These examples highlight the practical need to develop a fundamental understanding of the rheology and thermodynamics of liquid crystalline mixtures, and the formulation of mixture rules. Accurate mixture rules[3] for nematic fluids will be required to design fluids with specific rheological and flow-alignment behavior.

Viscoelasticity is a fundamental property that affects product performance, as in electro-optical devices[4], and processing performances as in the spinning of mesophase carbon fibers.[5] A widely used tool for viscoelastic characterization is the small amplitude oscillatory shear flow[6] through the measurements of the dynamic storage modulus (G') and the dynamic loss modulus (G''), the former indicating the elastic component and the latter the dissipative component of the shear modulus; an equivalent set of viscoelastic material functions is given by the dynamic viscosities $\eta' = G''/\omega$ and $\eta'' = G'/\omega$.

The elastic modes of single component nematic liquid crystals arise from director gradients (Franks elasticity) and from departures of the order parameters[7] from their equilibrium values (molecular elasticity). For nematic mixtures a third type of elasticity

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arises from relative rotations of the directors corresponding to the mixture components.[8] For example, a stable uniaxial nematic mixture of two rod-like nematics will store elastic energy when the angle between the two directors is non-zero. We refer to this type of elasticity as mixture elasticity.

As other elastic properties of nematics,[4] the mixture elasticity is a function of composition, temperature, and single component characteristics such as molecular weights, and molecular shapes. For synthetic nematic polymers, where polydispersity is the rule,[6] mixture elasticity arises naturally from molecular weights distributions. Although Frank and molecular elastic moduli have been characterized,[7] more work on mixture elasticity remains to be done.

Studies[9,10] of linear viscoelasticity in the presence of Frank elasticity show that at high and low frequencies single component nematics essentially behave as viscous fluids, and at intermediate frequencies close to the reciprocal relaxation time the nematic liquid crystal is viscoelastic. In this case η' exhibits the typical low and high frequency plateaus, while η'' exhibits a Lorentzian peaking at a frequency $\omega = 1/\tau_F$, where $\tau_F = K h^2/\mu$ is the relaxation time, K is a representative Frank elastic constant, h is the sample thickness, and μ is a characteristic viscosity. On the other hand studies[11] of viscoelasticity of single component nematics in the presence of molecular elasticity show essentially the same behavior as with the Frank elasticity, with η'' peaking at a frequency $\omega = 1/\tau_M$, where $\tau_M = L/\mu$ is the relaxation time, L is molecular elastic modulus (energy/volume) and μ is a characteristic viscosity. For nematic polymers and low molar mass nematics approaching the nematic-isotropic transition temperature $\tau_F < \tau_M$, and the Lorentzian peak in η'' due to Frank elasticity will occur at lower frequencies than the one due to molecular elasticity. In this paper we wish to characterize the corresponding viscoelastic behavior arising from mixture elasticity.

The objective of this paper is: (i) to present a macroscopic mechanical theory for nematic mixtures; (ii) to predict the linear viscoelasticity of single-phase uniaxial nematic mixtures of rod-like mesogens, and (iii) to characterize the composition and frequency dependence of the nematic viscoelasticity arising from mixture elasticity. We restrict the main discussion to: (i) uniaxial single-phase homogeneous nematic mixtures of two miscible uniaxial rod-like nematic liquid crystals, and (ii) homogeneous flows. We assume that the two nematic fluids are always perfectly miscible (i.e flow does not induce phase separation).

The paper is organized as follows. Section 2 develops the governing macroscopic rheological equations for homogeneous binary nematic mixtures and identifies the main parameters that control the alignment properties of the mixture. Section 3.1 analyses the director dynamics of the binary mixture when subjected to small amplitude rectilinear oscillatory shear. Section 3.2 presents the frequency and composition dependence of the storage G' and loss G'' dynamic moduli and the frequency dependence of the dynamic viscosity. Section 4 gives the conclusions.

2. MACROSCOPIC DYNAMICS OF HOMOGENEOUS BINARY NEMATIC MIXTURES

The specification of the average orientation of the rigid mesogens in a homogeneous binary nematic mixture composed of two uniaxial nematic liquid crystals is given by

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two vectors ($\mathbf{n}, \mathbf{m}$), known as the directors, and restricted by

$$\mathbf{n}\cdot\mathbf{n} = 1; \quad \mathbf{m}\cdot\mathbf{m} = 1 \tag{1a,b}$$

where in general $\mathbf{m}\cdot\mathbf{n} \neq 0$. For rod-like nematics the director represents the average orientation of the molecular unit vectors along the largest molecular dimension. For binary mixtures of two rod-like nematics we shall assume stable uniaxiality ($\mathbf{n}\cdot\mathbf{m} = 1$) in the absence of flow.

An approximate expression for the excess free energy density F as a function of the two directors ($\mathbf{n}, \mathbf{m}$), due to spatially homogeneous deformations, is given by:[8]

$$F = \frac{\kappa}{2}(\mathbf{n}\cdot\mathbf{m})^2 \tag{2}$$

where is κ is a temperature dependent phenomenological parameter whose units are energy/volume. The parameter κ is the static coupling coefficient between the two directors. For rod-rod binary mixtures $\kappa < 0$, the stable state in the absence of flow is uniaxial and the two directors are collinear, $\mathbf{n} = \mathbf{m}$; in the limit $\kappa \rightarrow -\infty$ the nematic liquid crystal is always uniaxial, but for finite values of κ an externally imposed flow may induce biaxiality, and Eq. (2) gives the stored elastic energy density due to flow-induced biaxiality.

The component concentration in a single-phase binary nematic mixture can be defined in terms of mole fractions (X) or volume fractions (Φ). The correct concentration to describe material properties for miscible mixtures will depend on the type of property.[3] For mixtures of low-molar mass nematics mole fractions are typically used[4] for properties such as viscosity and Frank moduli that depend on the number of molecular interactions. For single phase polymer mixtures volume fractions are the appropriate concentration variable. Without loss of generality we use throughout volume fraction as the concentration unit of each component of the binary mixture and note that to convert mole fractions X into volume fractions Φ we can use:

$$\frac{1}{X_1} = \frac{1}{\Phi_1} - \frac{w_2}{w_1}\left(\frac{\rho_1}{\rho_2} - \frac{M_1}{M_2}\right) \tag{3}$$

where the subscript 1 (2) refer to component 1 (2), w_1 (w_2) is the total mass of component 1 (2), ρ_1 (ρ_2) is the mass density of component 1 (2), and M_1 (M_2) is the molecular weight of component 1(2). To simplify the notation we use throughout $\Phi_1 = \Phi$ and $\Phi_2 = 1 - \Phi$. Below we use the following notation: $\Phi(1 - \Phi)$ is the volume fraction of the nematic component with director $\mathbf{n}(\mathbf{m})$.

The presence of mixture elasticity gives rise to the following molecular fields:[7]

$$h_i = -(\delta_{ij} - n_i n_j)\frac{\partial F}{\partial n_i} = -\kappa(\mathbf{n}\cdot\mathbf{m})[m_i - (\mathbf{n}\cdot\mathbf{m})n_i] \tag{4a}$$

$$H_i = -(\delta_{ij} - m_i m_j)\frac{\partial F}{\partial m_i} = -\kappa(\mathbf{n}\cdot\mathbf{m})[n_i - (\mathbf{n}\cdot\mathbf{m})m_i] \tag{4b}$$

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The product of temperature with the rate of entropy production density, Δ, is given by the following difference between dissipative and storing elastic processes:

$$\Delta = \mathbf{t}^s\mathbf{:D} + \Phi\,\mathbf{h\cdot N} + (1-\Phi)\,\mathbf{H\cdot M} \tag{5}$$

where $\mathbf{t}^s$ is the symmetric traceless extra stress tensor. The fluxes are the rate of symmetric viscous extra stress tensor $\mathbf{t}^s$ and the products of the mole fractions times the Jaumann derivatives[6] of the directors $\mathbf{N}$ and $\mathbf{M}$, given by:

$$N_i = \dot{n}_i - W_{ij}n_j;\ M_i = \dot{m}_i - W_{ij}\,m_j;\ W_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right) \tag{6a,b,c}$$

where $\mathbf{v}$ is the velocity vector, $\mathbf{W}$ is the antisymmetric vorticity tensor and the superposed dot denotes material differentiation. The constraints $\mathbf{n\cdot N} = 0$ and $\mathbf{m\cdot M} = 0$ arise due to the unit length constraint on the directors ($\mathbf{n\cdot n} = 1$, $\mathbf{m\cdot m} = 1$). The forces appearing in Eq. (5) are the symmetric traceless rate of deformation tensor $\mathbf{D}$ and the two vector molecular fields $\mathbf{h}$ and $\mathbf{H}$ with the former given by:

$$D_{ij} = \frac{1}{2}\left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right] \tag{7}$$

Note that in Eq. (5) terms arising from interdiffusion and concentration gradients are not included because we are considering homogeneous flows. A linear expansion of the fluxes $\{\mathbf{t}^s, \Phi\mathbf{N}, (1-\Phi)\mathbf{M}\}$ in terms of the forces $\{\mathbf{D}, \mathbf{h}, \mathbf{H}\}$ gives the following constitutive equations for the fluxes:

$$\begin{aligned}
\mathbf{t}^s = {} & \Phi\,[2\,\nu\,\mathbf{D} + \alpha_1\,\mathbf{nn}(\mathbf{nn:D}) + \alpha_2\,(\mathbf{nn\cdot D} + \mathbf{D\cdot nn})] \\
& + (1-\Phi)\,[2\,\nu\,\mathbf{D} + \beta_1\,\mathbf{mm}(\mathbf{mm:D}) + \beta_2\,(\mathbf{mm\cdot D} + \mathbf{D\cdot mm})] \\
& + \Phi(1-\Phi)\,\xi\,(\mathbf{nn}(\mathbf{D:mm}) + \mathbf{mm}\,(\mathbf{D:nn}) + 2\mathbf{nm}\,(\mathbf{D:nm}) \\
& + 2\,\mathbf{mn}\,(\mathbf{D:nm})) - \Phi\left[\frac{\lambda^n}{2}(\mathbf{nh} + \mathbf{hn}) + \frac{\Lambda^{nm}}{2}\mathbf{m\cdot h}\,(\mathbf{nm} + \mathbf{mn})\right] \\
& - (1-\Phi)\left[\frac{\lambda^m}{2}(\mathbf{mH} + \mathbf{Hm}) + \frac{\Lambda^{mn}}{2}\mathbf{n\cdot H}\,(\mathbf{mn} + \mathbf{nm})\right] \\
\Phi\mathbf{N} = {} & \Phi\,\lambda^n\,[\mathbf{D\cdot n} - (\mathbf{D:nn})\mathbf{n}] \\
& + \Phi(1-\Phi)\left[\Lambda^{nm}(\mathbf{D:nm}) - \frac{\kappa}{\gamma_1^n}(\mathbf{n\cdot m})\right][\mathbf{m} - (\mathbf{n\cdot m})\,\mathbf{n}\,] \\
(1-\Phi)\mathbf{M} = {} & (1-\Phi)\lambda^m[\mathbf{D\cdot m} - (\mathbf{D:mm})\,\mathbf{m}] \\
& + \Phi(1-\Phi)\left[\Lambda^{mn}(\mathbf{D:nm}) - \frac{\kappa}{\gamma_1^m}(\mathbf{n\cdot m})\right][\mathbf{n} - (\mathbf{n\cdot m})\,\mathbf{m}]
\end{aligned} \tag{8a, b, c}$$

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where μ, $\{\alpha_i\}$, $\{\beta_i\}$ are viscosities, λ^n and λ^m are dimensionless reactive parameters, Λ^{nm} and Λ^{mn} are dimensionless reactive parameters arising due to dynamic couplings, and γ_1^n and γ_1^m are the rotational viscosities for **n** and **m** respectively; we shall assume that these parameters are temperature independent. The ratios $\gamma_1^n/|\kappa|$ and $\gamma_1^m/|\kappa|$ are the two director relaxation times of the model. For this particular model the viscous stress is symmetric. We recall that for rod-like nematics the single component reactive parameters are non-negative:[7]

$$\lambda^n \geqslant 0, \quad \lambda^m \geqslant 0 \tag{9a,b}$$

The shear alignment properties of single-component rod-like nematics are dictated by the magnitude of the reactive parameter λ, and the following two cases arise:[7]

$$\text{Non-Aligning: } 0 \leqslant \lambda < 1, \quad \text{Aligning: } \lambda \geqslant 1 \tag{10a,b}$$

For binary mixtures the alignment in steady shear (not studied in this paper) will depend on concentration (Φ), the four reactive parameters (λ^n, λ^m, Λ^{nm}, Λ^{mn}), and the two relaxation times ($|\tau|/\gamma_1^n$, $|\tau|/\gamma_1^m$) appearing in Eq. (8b, c).

As is well known,[7] thermodynamic restrictions do not fix the signs of the four reactive parameters (λ^n, λ^m, Λ^{nm}, Λ^{mn}), with the consequence that these degrees of freedom give rise to a variety of alignment modes and transitions. The dynamical coupling terms Λ^{nm} and Λ^{mn} are analogous to the hydrodynamic interaction terms considered in polymer dynamics[6] and they may promote or hinder flow-alignment during shear. On the other hand the elastic storage mechanism, introduced by κ, and arising from mesogenic interactions between the two nematics always promotes uniaxiality if $\kappa < 0$. Dotting Eq. (8b) with **n** yields $\mathbf{N}\cdot\mathbf{n} = 0$, and dotting (8c) with **m** yields $\mathbf{M}\cdot\mathbf{m} = 0$, as required. In addition Eqs. (9) show that $\mathbf{N}(\mathbf{n}) = -\mathbf{N}(-\mathbf{n})$ and $\mathbf{M}(\mathbf{m}) = -\mathbf{M}(-\mathbf{m})$, as required. By setting $\Phi = 1$ in Eqs. (8), it is straightforward to show that the director model properly reduces to the well known viscous TIF model[12] applicable to single component low molar mass nematics and containing a single reactive parameter.

3. LINEAR VISCOELASTICITY OF BINARY NEMATIC MIXTURES

This section presents the predictions of the theory (Eqs. (8)) for small amplitude rectilinear oscillatory shear flow between to parallel plates of single phase uniaxial, incompressible, binary nematic mixtures under isothermal conditions. We refer the reader to[6] for other linear viscoelastic theories for isotropic polymer solutions and melts.

3.1 Director Dynamics in Small Amplitude Oscillatory Shear

Assume a known incompressible rectilinear small amplitude oscillatory shear flow given by:

$$\gamma_{yx} = \gamma_0 \sin(\omega t), \quad D_{yx} = \frac{\partial \gamma_{yx}}{\partial t} \gamma_0 \omega \cos(\omega t) \tag{11a,b}$$

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where γ_{yx}, D_{yx} are the yx components of the strain (displacement) tensor and deformation rate tensor, respectively. Here ω is the frequency of the sinusoidally oscillating plate and γ_0 is its small amplitude. In this geometry x is the flow direction, the x–y plane is the shear plane and z is along the vorticity direction. In the linear regime the two director fields (**n** and **m**) are parametrized without loss of generality as follows:

$$\mathbf{n} = (n_x, n_y, n_z) = (1, \theta_1, 0), \quad \mathbf{m} = (m_x, m_y, m_z) = (1, \theta_2, 0) \tag{12a,b}$$

where positive angles are measured anti-clockwise. Linearization around any other direction is straightforward. Replacing (11) and (12) into the governing Eqs. (8) we obtain the following linearized governing equations for θ_1 and θ_2:

$$\frac{d\theta_1}{dt} = D_{yx}[\lambda^n - 1] + (1 - \Phi)\frac{|\kappa|}{\gamma_1^n}(\theta_2 - \theta_1) \tag{13a}$$

$$\frac{d\theta_2}{dt} = D_{yx}[\lambda^m - 1] - \Phi\frac{|\kappa|}{\gamma_1^m}(\theta_2 - \theta_1) \tag{13b}$$

The relaxation times appearing in the coupled director oscillator system are:

$$\tau^n = \frac{\gamma_1^n}{|\kappa|}; \quad \tau^m = \frac{\gamma_1^m}{|\kappa|}; \quad \tau^{\text{mix}} = \Phi\tau^n + (1 - \Phi)\tau^m; \quad \tau = \frac{\tau^n\tau^m}{\tau^{\text{mix}}} \tag{14a,b,c,d}$$

where τ^n, τ^m are the single component relaxation times for rotations of **n** and **m**, τ^{mix} is the concentration dependent mixture relaxation time for the oscillators driven in series and τ is the concentration dependent mixture relaxation time for the oscillators driven in parallel. The most efficient way to analyze coupled oscillators is to find the normal coordinates of the system, that is to find the coordinates for which the coupled equations become uncoupled. The two normal coordinates for the coupled director oscillators are:

$$\psi_1 = \theta_1 - \theta_2; \quad \psi_2 = \frac{\Phi}{\tau^m}\theta_1 + \frac{(1 - \Phi)}{\tau^n}\theta_2 \tag{15a,b}$$

Substituting Eqs. (15) into Eqs. (13) and integrating we find that the normal coordinate ψ_1 is given by:

$$\psi_1 = (\theta_1 - \theta_2) = A_1\cos(\omega t + \varphi_1) \tag{16a}$$

$$A_1 = \gamma_0\lambda^{nm}\left[\frac{\omega\tau(1 + \omega\tau)}{1 + (\omega\tau)^2}\right]; \quad \tan\varphi_1 = -\omega\tau \tag{16b,c}$$

where

$$\lambda^{nm} = \lambda^n - \lambda^m \tag{17}$$

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and the normal coordinate ψ_2 by:

$$\psi_2 = \frac{\Phi}{\tau^m}\theta_1 + \frac{(1-\Phi)}{\tau^n}\theta_2 = A_2\cos(\omega t + \varphi_2) \tag{18a}$$

$$A_2 = \gamma_0 \frac{\tau^n\Phi(\lambda^n - 1) + \tau^m(1-\Phi)(\lambda^m - 1)}{\tau^n\tau^m}; \quad \varphi_2 = -\pi/2 \tag{18b,c}$$

The two modes of the system therefore are:

Biaxial Mode 1: $\psi_1 \neq 0; \psi_2 = 0$

Uniaxial Mode 2: $\psi_1 = 0; \psi_2 \neq 0$

Mode 1 is a biaxial mode since $\theta_1 - \theta_2 \neq 0$, and the two directors **n** and **m** are not collinear. Mode 2 is a uniaxial mode since $\theta_1 - \theta_2 = 0$, and the two directors **n** and **m** are collinear. The characteristics of the two modes are as follows:

(i) Biaxial Mode 1 ($\psi_1 \neq 0; \psi_2 = 0$). The biaxial mode 1 is present when the following two restrictions hold:

$$\lambda^{nm} = \lambda^n - \lambda^m \neq 0; \quad \tau = \frac{\tau^n(\lambda^n - 1)}{(1-\Phi)\lambda^{nm}} = -\frac{\tau^m(\lambda^m - 1)}{\Phi\lambda^{nm}} \tag{19a,b}$$

the restrictions arising from the constraints $\psi_1 \neq 0, \psi_2 = 0$. Using these two restrictions in Eqs. (16) we find the following expressions for the two distinct director angles:

$$\theta_1 = \left(\frac{\lambda^n - 1}{\lambda^{nm}}\right)\psi_1; \quad \theta_2 = \left(\frac{\lambda^m - 1}{\lambda^{nm}}\right)\psi_1; \quad \theta_2 = \left(\frac{\lambda^m - 1}{\lambda^n}\right)\theta_1 \tag{20a,b,c}$$

Since the relaxation time is positive ($\tau > 0$), the restriction (19b) imposes the following inequalities on the reactive parameters:

$$\lambda^n > 1, \lambda^m < 1 \text{ or } \lambda^n < 1, \lambda^m > 1 \tag{21}$$

which means that the biaxial mode 1 is obtained by mixing flow-aligning ($\lambda > 1$) with non-aligning nematics ($0 < \lambda < 1$).

(i) Uniaxial Mode 2 ($\psi_1 = 0, \psi_2 \neq 0$). The uniaxial mode 2 is present when the following two restrictions hold:

$$\lambda^{nm} = \lambda^n - \lambda^m = 0; \quad \tau \neq \frac{\tau^n(\lambda^n - 1)}{(1-\Phi)\lambda^{nm}} \neq -\frac{\tau^m(\lambda^m - 1)}{\Phi\lambda^{nm}} \tag{22a,b}$$

the restrictions arising from the constraints $\psi_1 = 0, \psi_2 \neq 0$. Using these two restrictions we find the following simplified expressions for the mode's amplitude and for the single

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director angle:

$$A_2 = \gamma_0 \frac{(\lambda - 1)}{\tau}; \quad \lambda = \lambda^n = \lambda^m \tag{23a,b}$$

$$\theta_1 = \theta_2 = \tau \psi_2 = \gamma_0 (\lambda - 1) \sin(\omega t) \tag{23c}$$

The uniaxial mode 2 is obtained by mixing two nematics of equal reactive parameters.

Figure 1 shows the schematics of the two director's dynamics in the presence of the small amplitude oscillatory shear for the biaxial mode 1 (Fig. 1a) and for the uniaxial mode 2 (Fig. 1b); the bottom arrow indicates the direction of increasing time. Figure 1a shows that the biaxial mode has the following four representative cases: (a) two single oscillator modes either when $\lambda^n > 1$, $\lambda^m = 1$, or when $\lambda^m > 1$, $\lambda^n = 1$. In the former case **m** is fixed and **n** oscillates, while in the latter case **n** is fixed and **m** oscillates; (b) two anti-phase coupled oscillator modes either when $\lambda^n > 1$, $\lambda^m = 1$, or when $\lambda^m > 1$, $\lambda^n < 1$; these modes are designated by $(+\ -)$ and $(-\ +)$, respectively. In the former case the amplitude of **n** is larger than that of **m**, and in the latter the amplitude inequality is reversed. From Eqs. (20, 21) it follows that:

$$\mathrm{sign}(\theta_1) = -\mathrm{sign}(\theta_2) \tag{24}$$

and therefore the biaxial mode is an anti-phase mode. Figure 1b shows the in-phase oscillations of **n** and **m** in mode 1 that occur whenever $\lambda^n = \lambda^m$.

Figure 2 shows a 2-D projection of the parameter space indicating the parametric regions for the two modes as a function of λ^n and λ^m. The figure shows that the uniaxial mode 2 (dashed line) may occur with aligning or non-aligning nematics. As mentioned above, the biaxial mode 1 may occur when mixing aligning with non-aligning materials.

Figure 3 shows the scaled director orientation $\bar{\theta}_2 = \theta_2/\gamma_0$ as a function of the scaled director orientation $\bar{\theta}_1 = \theta_1/\gamma_0$, for ψ_1 ($\lambda^n = 1$, $\lambda^m = 2$) and ψ_2 ($\lambda^n = \lambda^m$). The horizontal and vertical full lines correspond to the single oscillator mode ($\lambda^n = 1$ or $\lambda^m = 1$). The arrows show the oscillatory director motion due to imposed strain oscillations.

The frequency dependence of the amplitudes (A_1, A_2) and phases (φ_1, φ_2) of the two normal coordinates are found from Eqs. (16, 19). For ψ_1 we find:

$$\lim_{\omega\tau \to 0} \varphi_1 = 0; \quad \lim_{\omega\tau \to \infty} \varphi_1 = -\pi/2 \tag{25a,b}$$

$$\lim_{\omega\tau \to 0} A_1 = 0; \quad \lim_{\omega\tau \to \infty} A_1 = \gamma_0 \lambda^{nm} \tag{25c,d}$$

For large frequencies ψ_1 becomes in-phase with the imposed strain oscillations with an amplitude that scales with λ^{nm}. On the other hand the amplitude A_2 and phase φ_2 of ψ_2 are independent of frequency. Figure 4 shows the scaled amplitudes and phases of mode 1 (full line) and mode 2 (dashed line); the amplitudes are scaled as follows: $A_1/(\gamma_0 \lambda^{nm})$, and $A_2/(\gamma_0 \lambda^n)$. The figure shows that only at some intermediate frequencies an out-phase (with respect to strain) component with considerable amplitude is found. Figure 5 shows the scaled amplitude of the out-of-phase (full line) and in-phase

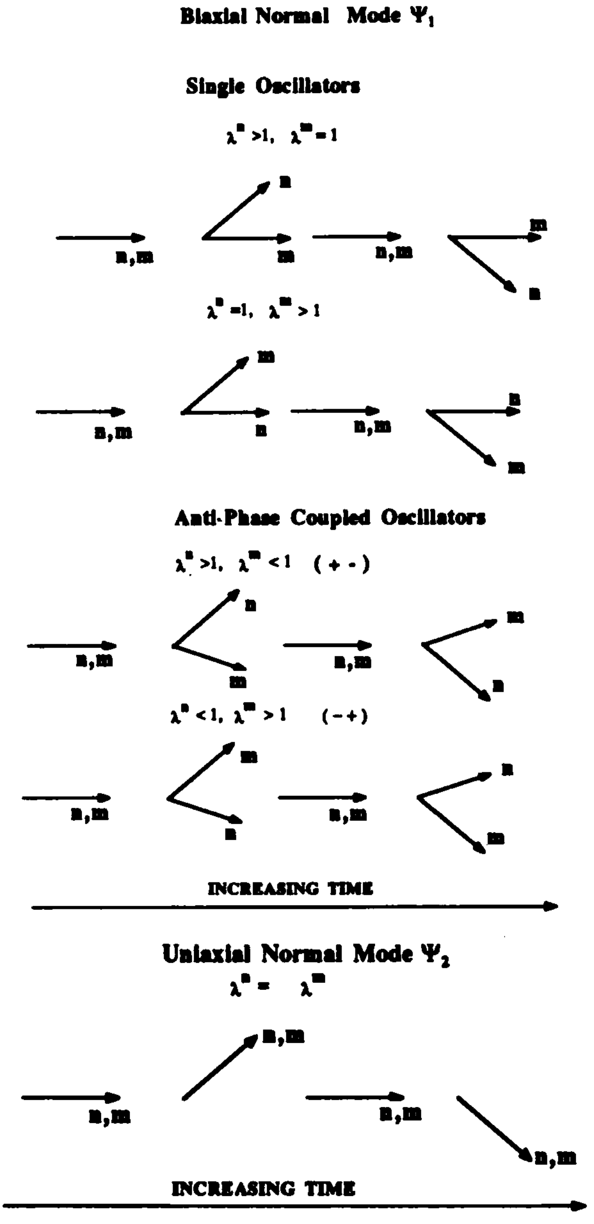

FIGURE 1 Schematics of the two director's (n and m) dynamics in the presence of small amplitude rectilinear oscillatory shear, for the biaxial mode 1 (Fig. 1a) and for the uniaxial normal mode 2 (Fig. 1b); the bottom arrow indicates the direction of increasing time. The biaxial mode has: (a) two single oscillator modes ($\lambda^n > 1, \lambda^m = 1$ or $\lambda^m > 1, \lambda^n = 1$); (b) two antiphase coupled oscillator modes ($\lambda^n > 1, \lambda^m < 1$ or $\lambda^m > 1, \lambda^n < 1$).

(dashed-dot line) components of mode 1 as a function of the scaled frequency $\omega\tau$, where the amplitudes are scaled with $\gamma_0\lambda^{nm}$. We recall that the reference phase is that of strain oscillations. (see Eq. (11a)). The in-phase component plateaus at high frequency $\omega = 1/\tau$.

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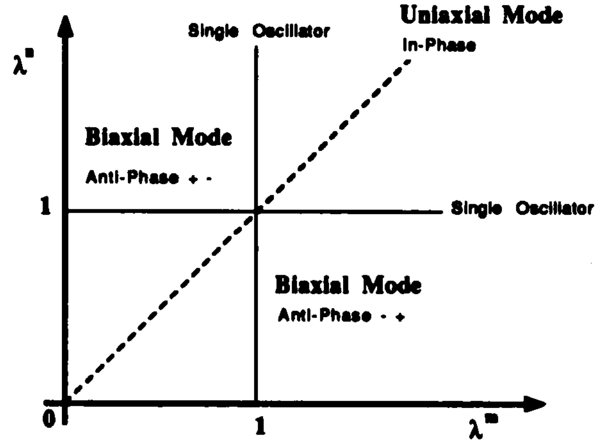

FIGURE 2 2-D projection of the parameter space indicating the parametric regions for the biaxial and uniaxial modes as a function of λ^n and λ^m. The figure shows that the uniaxial mode 2 (dashed line) may occur with aligning or non-aligning nematics. On the other hand the biaxial mode 1 may occur when mixing aligning with non-aligning materials.

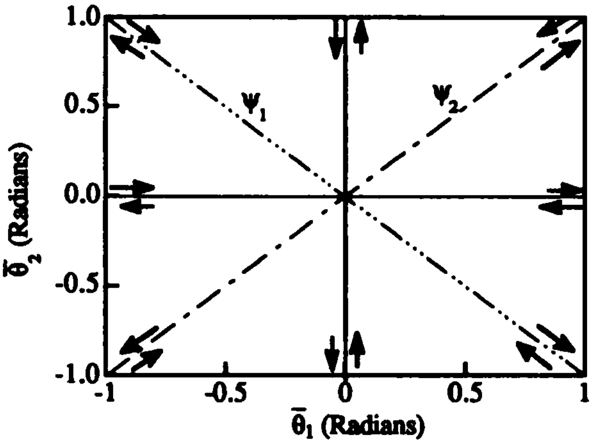

FIGURE 3 Scaled director orientation $\bar{\theta}_2 = \theta_2/\gamma_0$ as a function of the scaled director orientation $\bar{\theta}_1 = \theta_1/\gamma_0$. for $\psi_1(\lambda^n = 1, \lambda^m = 2)$ and $\psi_2(\lambda^n = \lambda^m)$. The horizontal and vertical full lines correspond to the single oscillator modes ($\lambda^n = 1$ or $\lambda^m = 1$). The arrows show the oscillatory director motion due to the imposed strain oscillations.

The concentration dependence of the modes follow directly from Eqs. (19). For a given pair of nematics (λ^n and λ^m), the biaxial mode 1 is found only at a volume fraction of

$$\Phi = \frac{-\tau^m(\lambda^m - 1)}{\tau^n(\lambda^n - 1) + \tau^m(\lambda^m - 1)} \tag{26}$$

On the other hand, according ot Eqs. (22, 23), the uniaxial mode 2 is concentration independent.

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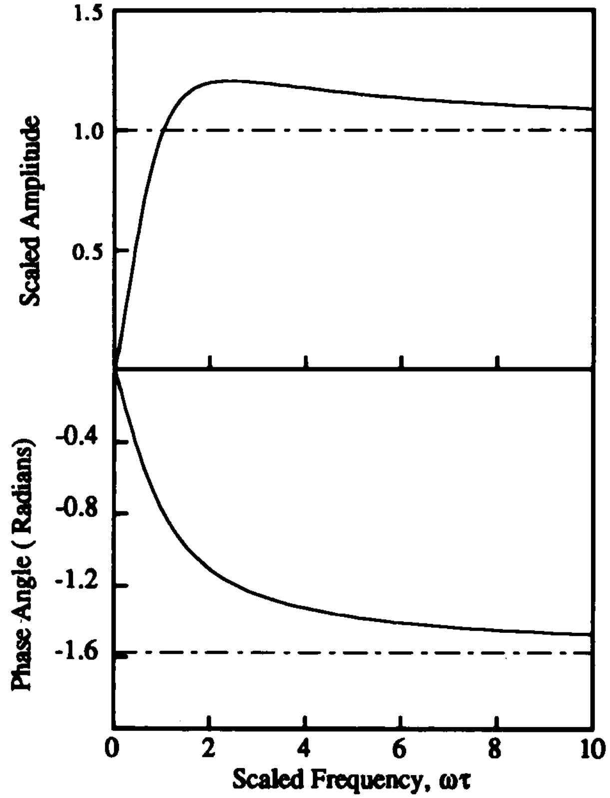

FIGURE 4 Scaled amplitudes and phases of mode 1 (full line) and mode 2 (dashed line); the amplitudes are scaled as follows: $A_1/(\gamma_0\lambda^{nm})$, and $A_2/(\gamma_0\lambda^n)$. The figure shows that only at some intermediate frequencies an out-phase (with the strain) component with considerable amplitude is found.

Finally, the director's oscillatory properties of arbitrary mixtures subjected to small amplitude oscillatory mixtures can be found using the following linear combinations of the normal coordinates:

$$\theta_1 = (1 - \Phi)\frac{\tau}{\tau^n}\psi_1 + \tau\psi_2 \tag{27a}$$

$$\theta_2 = -\Phi\frac{\tau}{\tau^m}\psi_1 + \tau\psi_2 \tag{27b}$$

were the unrestricted normal coordinate values for ψ_1 and ψ_2 are used (see Eqs. (16, 18)). For example, for the infinitely dilute solution $\Phi \to 0$, we find that:

$$\frac{\theta_1}{\gamma_0} = \left[\frac{\lambda^{nm}\omega\tau}{1 + (\omega\tau)^2}\right]\cos\omega\tau + \left[(\lambda^n - 1) - \frac{\lambda^{nm}}{1 + (\omega\tau)^2}\right]\sin\omega\tau \tag{28a}$$

$$\frac{\theta_2}{\gamma_0} = (\lambda^m - 1)\sin\omega\tau \tag{28b}$$

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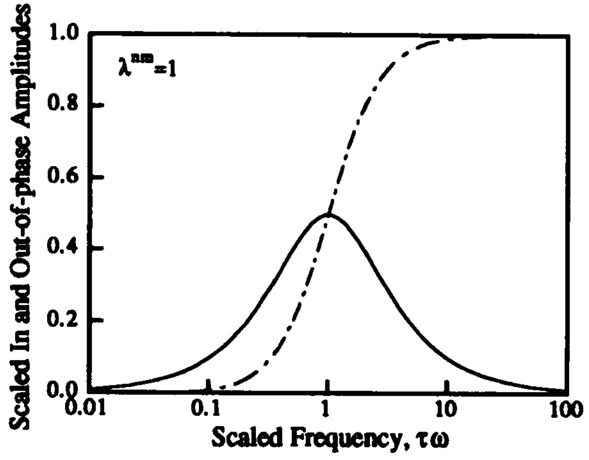

FIGURE 5 Scaled amplitude of the out-of-phase (full line) and in-phase (dashed-dot line) components of mode 1 as a function of the scaled frequency $\omega\tau$, where the amplitudes are scaled with $\gamma_0\lambda^{nm}$. We recall that the reference phase is that of the strain oscillations. (Eq. (11a)). The in-phase component plateaus at high frequency. The out-of-phase component peaks at the resonance frequency $\omega = 1/\tau$.

Thus at small frequencies the dilute mixture is uniaxial and in-phase with the strain, but at large frequencies it is biaxial and out-of-phase with the strain.

3.2 Linear Viscoelastic Material Functions for Binary Nematic Mixtures

This section presents and analyzes the dynamic storage G' and loss G'' moduli, and the real η' and an imaginary η'' components of the dynamic viscosity of a binary nematic mixture subjected to rectilinear small amplitude oscillatory shear. The frequency and concentration dependence of the dynamic moduli is also analyzed. It should be mentioned that these material functions can be expected to be useful in : (i) finding the mixture time constant, (ii) characterizing the difference between reactive parameters $\lambda^n - \lambda^m$, (iii) characterizing the molecular weights of the mixture, (iv) determining the relative importance of Frank, molecular, and mixture elasticities, and (v) characterizing polydispersity in polymer nematics.

Substituting Eqs. (11) into Eq. (8a) the yx component of the extra stress tensor is given by:

$$t_{yx} = \Phi t^n_{yx} + (1-\Phi) t^m_{yx} + \Phi(1-\Phi) t^e_{yx} \tag{29a}$$

$$t^n_{yx} = (2\mu + \alpha_2) D_{yx}; \quad t^m_{yx} = (2\mu + \beta_2) D_{yx}; \quad t^e_{yx} = \frac{|\kappa|\lambda^{nm}}{2}\psi_1 \tag{29b}$$

where t^n_{yx}, t^m_{yx} are contributions to the viscous stresses from the two nematic components, and where t^e_{yx} is the elastic stress arising from flow-induced biaxiality. Note that only the normal coordinate ψ_1 contributes to the elastic stress. The mechanical model

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corresponding to Eq. (29) is a viscous dashpot in parallel with a Maxwell element. The viscous dashpot represents the viscous dissipation due to positional motion. The spring in the Maxwell element represents the mixture elasticity, while the dashpots elements represent the dissipation of **n** and **m**. A similar separation into viscous and elastic stresses occurs when considering viscoelasticity with Frank elasticity,[9,10] and with molecular elasticity.[11] The elastic stress obeys the following differential equation:

$$t^e_{yx} + \tau \frac{dt^e_{yx}}{dt} = \Phi(1-\Phi)|\kappa|(\lambda^{nm})^2 \tau D_{yx} \tag{30}$$

Assuming that the harmonic oscillatory strain ($\gamma_{yx} = \gamma_0 e^{i\omega t}$) produces a harmonic stress response ($t^e_{yx} = t^s_0 e^{i\omega t}$), and using the standard definition[6] for the complex modulus $G(t^s_{yx} = G\gamma_{yx} = (G' + iG'')\gamma_{yx})$ we find the following expressions for the storage G' and loss modulus G'' of the binary nematic mixture:

$$G' = \Phi(1-\Phi)\frac{|\kappa|(\lambda^{nm})^2(\omega\tau)^2}{1+(\omega\tau)^2} \tag{31a}$$

$$G'' = \Phi[2\mu + \alpha_2]\omega + (1-\Phi)[2\mu + \beta_2]\omega + \Phi(1-\Phi)\frac{|\kappa|(\lambda^{nm})^2\omega\tau}{1+(\omega\tau)^2} \tag{31b}$$

The mixture elasticity contributes to both G' and G'', and the purely viscous component appears only in G'' (the first two terms in Eq. (31b)). We recall that the expressions for the real η' and imaginary η'' components of the complex viscosity η are given by: $\eta' = G''/\omega$ and $\eta'' = G'/\omega$. Scaling with $|\kappa|$, the real $\bar{\eta}'$ and imaginary $\bar{\eta}''$ components of the dynamic viscosity are given by:

$$\bar{\eta}' = \bar{\eta}(\infty) + \frac{[\bar{\eta}(0) - \bar{\eta}(\infty)]}{1+(\omega\tau)^2} \tag{32a}$$

$$\bar{\eta}' = \frac{[\bar{\eta}(0) - \bar{\eta}(\infty)]\,\omega\tau}{1+(\omega\tau)^2} \tag{32b}$$

where

$$\bar{\eta}(0) = \Phi(1-\Phi)(\lambda^{nm})^2 + \Phi\frac{(2\mu+\alpha_2)}{|\kappa|\tau} + (1-\Phi)\frac{(2\mu+\beta_2)}{|\kappa|\tau} \tag{32c}$$

$$\bar{\eta}(\infty) = \Phi\frac{(2\mu+\alpha_2)}{|\kappa|\tau} + (1-\Phi)\frac{(2\mu+\beta_2)}{|\kappa|\tau} \tag{32d}$$

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The phase angle ϕ of the elastic storage is given by

$$\tan\phi = \frac{\bar{\eta}''}{\bar{\eta}'} = \omega\tau \tag{33}$$

Multiplying Eqs. (32a,b) by $\omega\tau$ yields the following scaled dynamic storage $\bar{G}'$ and loss $\bar{G}''$ moduli:

$$\bar{G}' = \bar{\eta}''\omega\tau = \frac{[\bar{\eta}(0) - \bar{\eta}(\infty)]\,(\omega\tau)^2}{1 + (\omega\tau)^2} \tag{34a}$$

$$\bar{G}'' = \bar{\eta}'\omega\tau = \bar{\eta}(\infty)\omega\tau + \frac{[\bar{\eta}(0) - \bar{\eta}(\infty)]\,\omega\tau}{1 + (\omega\tau)^2} \tag{34b}$$

Figure 6 shows the scaled moduli ($\bar{G}'$, $\bar{G}''$) and scaled dynamic viscosity ($\bar{\eta}'$, $\bar{\eta}''$) components as a function of the scaled frequency $\omega\tau$ for the following parametric

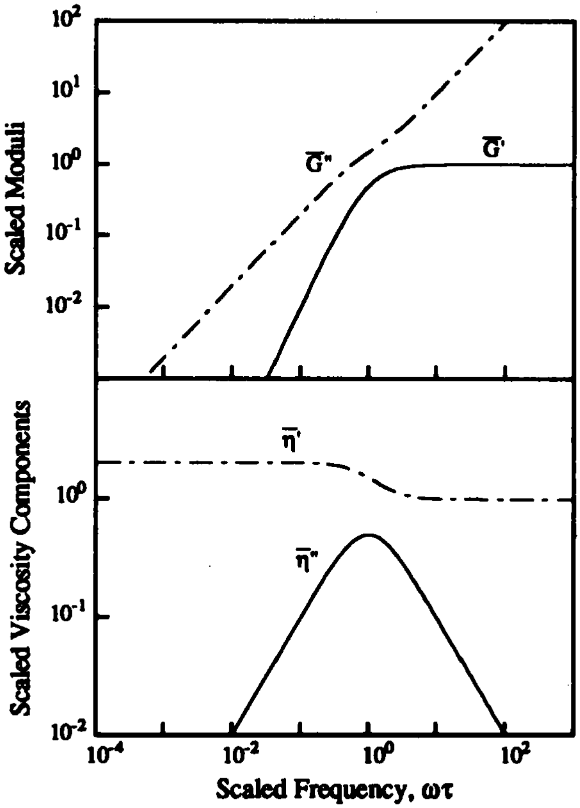

FIGURE 6 Scaled moduli ($\bar{G}'$, $\bar{G}''$) and scaled dynamic viscosity ($\bar{\eta}'$, $\bar{\eta}''$) components as a function of the scaled frequency $\omega\tau$, for the following parametric conditions: $\bar{\eta}(0) - \bar{\eta}(\infty) = 1$, $\bar{\eta}(\infty) = 1$. See text.

conditions: $\bar{\eta}(0) - \bar{\eta}(\infty) = 1$, $\bar{\eta}(\infty) = 1$. The upper figure shows that the scaled storage modulus $\bar{G}'$ plateaus at large scaled frequencies, while the scaled loss modulus $\bar{G}''$ is due to the purely.viscous contribution (the first two terms in Eq. (32b)). The plateau of $\bar{G}'$ at large frequencies is due to the saturation of the mixture elasticity with increasing frequency (see Fig. 4). The bottom figure shows that the real component of the dynamic viscosity $\bar{\eta}'$ exhibits the typical[6] low and high frequency plateaus, while the imaginary part peaks at $\omega\tau = 1$. The shape of $\bar{\eta}''$ shows that the nematic mixture is viscous at low and high scaled frequencies, and that it is viscoelastic at intermediate scaled frequencies. The phase angle (Eq. (33)) has a maximum at $\omega\tau = 1$, indicating the frequency at which elastic storage is most pronounced. Since τ is a function of Φ the viscoelastic behavior for a given set of single components can be tuned by varying the composition. The frequency dependence of the dynamic modulus and the dynamic viscosity reported here is essentially identical to those computed for single component nematic using Frank elasticity[9] and molecular elasticity[11] models. We would thus expect the presence of three characteristic frequencies as dictated by the magnitudes of the three types of orientation relaxations.

The limiting frequency dependence of G' and G'' can be obtained from Eqs. (31). The frequency scaling of the moduli is:

$$\lim_{\omega\to 0} G' \approx \omega^2; \quad \lim_{\omega\to\infty} G' \approx \text{constant} \tag{35a}$$

$$\lim_{\omega\to 0} G'' \approx \omega; \quad \lim_{\omega\to\infty} G'' \approx \omega \tag{35b}$$

The limiting concentration dependence can also be obtained from Eqs. (31). At infinitesimal frequencies the concentration scaling of the moduli is:

$$\lim_{\omega\to 0} G'' \approx \frac{\Phi(1-\Phi)}{[\tau^n\Phi + \tau^m(1-\Phi)]^2}; \quad \lim_{\omega\to 0} G'' \approx c\Phi + \frac{\Phi(1-\Phi)}{[\tau^n\Phi + \tau^m(1-\Phi)]} \tag{36a,b}$$

where c is a concentration independent factor. For a mixture of a low molar mass (τ^n) nematic with a nematic polymer ($\tau^m \gg \tau^n$) we find:

$$\lim_{\omega\to 0} G' \approx \frac{\Phi}{(1-\Phi)}; \quad \lim_{\omega\to 0} G'' \approx \Phi \tag{37}$$

which shows that G' may have a very sensitive concentration dependence in comparison to G''. At infinitely large frequencies the concentration scaling of the moduli is:

$$\lim_{\omega\to\infty} G' \approx \Phi(1-\Phi); \quad \lim_{\omega\to\infty} G'' \approx c\Phi \tag{38a,b}$$

where c is a concentration independent factor.

4. CONCLUSIONS

A macroscopic continuum mechanical model for incompressible homogeneous binary nematic mixtures under isothermal conditions has been presented. The model is an

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extension of Ericksen's Transversely Isotropic Theory.[12] The nematic mixture model accounts for the elasticity of the mixture that is assumed to be uniaxial in the absence of flow. The model equations for small amplitude oscillatory rectilinear shear predict the presence of two modes when the director is assumed to lie in the shear plane. A biaxial mode that contribute to the elastic stress is out-of-phase with the imposed oscillatory strain. A uniaxial mode that does not contribute to the elastic stress is in-phase with the strain. The linear viscoelasticity is pronounced at intermediate frequencies while at low and high frequencies the nematic mixture behaves as a viscous fluid in agreement with previous results using Frank elasticity[9] and molecular elasticity.[11] The composition dependence of the dynamic moduli is stronger at low frequency than at high frequency.

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