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Flow-alignment and viscosity rules for single-phase binary mesomorphic mixtures

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A macroscopic model for incompressible homogeneous (single phase) binary nematic mixtures, under isothermal conditions is given. The rheological model is a generalization of the standard Ericksen's nematorheological model for single component uniaxial rod-like nematic liquid crystals. Its special cases include single component orthorhombic biaxial nematics and single component uniaxial nematics. The theory is used to formulate rules for the rotational viscosity and the reactive parameter of nematic mixtures in the presence of weak flows. The predicted mixture rules for the reactive parameter and rotational viscosity are analysed as a function of concentration and rotational viscosity ratio for various monomeric and polymeric mixtures, and for rod–rod, disc–disc, and rod–disc nematic mixtures. The mixture rules are used to compute alignment phase diagrams and alignment transition (orientational instability) thresholds.

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 for nematic fluids will be required to design fluids with specific rheological and flow-alignment behaviour.

A fundamental rheological property of a nematic liquid crystal is its ability to orient close to the flow direction and in the shear plane when subjected to a shear flow. Nematics that display this property are known as flow-aligning nematics [3]. The flow-aligning angle for low molar mass uniaxial nematics is known as the Leslie angle and typically is less than 10°. Nematics that lack the ability to orient close to the shear flow direction are commonly known as non-aligning nematics. The parameter that describes shear flow-alignment is known as the reactive parameter $\lambda = -\gamma_2/\gamma_1$, where γ_1 is the rotational torque coefficient and γ_2 the irrotational torque coefficient. Frequently, alignment (orientation) transitions involving the loss or appearance of alignment are observed. Loss of alignment gives rise to complex orientation transient and stationary patterns [4, 5]. For single component nematic liquid crystals, shear flow-alignment is a rheological property that may depend on the magnitude of the shear rate [6], and temperature [3]. For low molar mass nematics, temperature is a tuning parameter for the loss of alignment through the creation at lower temperatures of fluctuating cybotactic clusters [3, 7]. On the other hand, for nematic polymers shear rate is an effective tuning parameter for the loss of alignment at lower shear rates through the production of a broad molecular distribution function [6, 8]. For miscible mesomorphic nematic mixtures we thus expect that concentration, temperature, shear rate, and molecular weight differences will be effective tuning parameters for alignment transitions in shear flows.

Previous work on the continuum mechanical theory of nematic liquid crystal mixtures [9, 10] was mainly directed to a formulation of balance laws, without consideration on proper types of constitutive equations for these structured mixtures. A more recent work on nematic mixtures [11] presents a macroscopic theory for biaxial binary mixtures of two uniaxial nematic liquid crystals and characterizes its shear flow-alignment and its response to magnetic fields. An important finding of this theoretical work is that due to dynamic interactions, the shear alignment angles of the directors of the biaxial mixture are a function of the shear rate, in contrast to truly single component biaxial nematics; as is well known director theories for liquid crystal flows predict a shear rate-independent alignment angles [3, 12, 13]. More recently a macroscopic theory for single-phase rod-like nematic mixtures has been given [14]; this work did not include concentration effects. In this work it was found that mixtures of two aligning nematics result in most cases in flow-aligning biaxial nematic mixtures, and that mixtures of an aligning nematic with a non-aligning nematic results in a flow-aligning biaxial nematic mixture, only if sufficient strong dynamic interactions are present. In all cases the predicted degree and type of alignment behaviour is shear rate-dependent.

The effect of concentration and temperature on the flow-alignment of low molar mass nematic mixtures has not been experimentally characterized. On the other hand, available rotational viscosity (γ_1) measurements on miscible nematic mixtures seem to indicate that interaction effects produce deviations from the typical linear mixing rules [15]. For example, the rotational viscosity of mixtures of polar azoxy compounds shows a local minimum at an intermediate mole fraction concentration [15]. Thus we would expect a similarly non-ideal mixture behaviour for the irrotational torque coefficient γ_2, and the reactive parameter λ.

Mixtures of polymeric and low molar mass nematics should give rise to alignment behaviour that is affected by both shear rate and temperature. Dilute homogeneous binary mixtures of aligning low-molar mass nematics with side chain nematic polymers, and non-aligning low-molar mass nematics with main chain nematic polymers have been extensively studied [16]. These experiments provide conclusive evidence that the rheology of nematic mixtures exhibits strong deviations from single component behaviour. For example, it was found that a dilute solution of a side chain nematic polymer in a non-aligning nematic gives rise to a flow-aligning homogeneous nematic mixture, and a dilute solution of a main chain nematic polymer in an aligning nematic gives rise to a non-aligning homogeneous nematic mixture. The alignment properties of the two dilute mixtures were explained using a model [17] that takes into account the modification of the isotropic shape of a flexible polymer coil in the presence of the nematic solvent; semi-dilute or concentrated solutions were not investigated.

From the above discussion it appears that there is a strong need to develop a better understanding of the rheology of nematic mixtures in general, and flow-alignment mixture rules in particular. With respect to the latter, an essential issue is to be able to derive mixture rules from knowledge of the components properties and their interactions. The objective of the present paper is (i) to present a macroscopic rheological equation of state for homogeneous binary nematic mixtures, (ii) use the theory to derive flow-alignment and rotational viscosity mixture rules applicable to weak flows, and (iii) to use the mixture rules to construct alignment phase diagram and to predict alignment transitions. We restrict our discussion to a model binary homogeneous mixture of two uniaxial nematic liquid crystals, and that is composed of two types of mesogenic molecules. We treat three types of binary rigid nematic mixtures involving the following molecular shapes: (i) rod–rod, (ii) disc–disc, and (iii) rod–disc. In this paper we generalize Ericksen's transversely isotropic theory (TIF) [18] for single component nematic liquids to a binary mixture. As common to all director theories, here we neglect any possible flow effect on the scalar order parameters [3], thus restricting the validity of the model predictions to materials and processing conditions for which the scalar order parameters are not significantly affected by flow.

The paper is organized as follows. § 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. § 3 presents the mixture rules (for the rotational viscosity and the reactive parameter) and alignment phase diagrams for uniaxial nematic mixtures composed of rod-like or disc-like molecules. § 4 presents the mixture rules (for the rotational viscosity and the reactive parameter) and alignment phase diagrams for biaxial nematic mixtures composed of rod-like with disc-like molecules. § 5 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 two vectors $(\mathbf{n}, \mathbf{m})$, known as the directors, restricted by

$$\mathbf{n}\cdot\mathbf{n} = 1; \quad \mathbf{m}\cdot\mathbf{m} = 1 \qquad (1\,a, b)$$

where in general $\mathbf{m}\cdot\mathbf{n} \neq 0$. For rod-like (disc-like) nematics the director represents the average orientation of the molecular unit vectors along the largest (shortest) molecular dimension. For binary mixtures of two rod-like nematics or two disc-like nematics we shall assume stable uniaxiality $(\mathbf{n}\cdot\mathbf{m} = 1)$ in the absence of flow. For binary mixtures of uniaxial rods with uniaxial discs we shall assume stable biaxiality $(\mathbf{n}\cdot\mathbf{m} = 0)$ 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 [11]

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

where the κ is a temperature dependent phenomenological parameter, whose units are energy/volume. The parameter κ is the static coupling coefficient between the two directors. The two representative cases are as follows. (i) For rod–rod and disc–disc 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 the flow may induce biaxiality, and equation (2) gives the stored elastic energy density due to flow-induced biaxiality. (ii) For rod–disc binary mixtures $\kappa > 0$, the stable state in the absence of flow is biaxial, and the two directors are orthogonal, $\mathbf{n} \cdot \mathbf{m} = 0$; in the limit $\kappa \rightarrow \infty$ the nematic liquid crystal is always perfectly biaxial, but for finite values of κ the flow may induce uniaxiality, and equation (2) gives the stored elastic energy density due to flow-induced uniaxiality.

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 for miscible mixtures will depend on the type of property. For mixtures of low molar mass nematics mole fractions are typically used [15] for properties, such as viscosity and Frank moduli, that depend on the number of molecular interaction. For single phase polymer mixtures volume fractions are the appropriate concentration variable. Without loss of generality we use throughout volume fraction as a 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 product of temperature with the rate of entropy production density, Δ, is given by the following difference between dissipative and storing elastic processes:

$$\Delta = \mathbf{t}^s : \mathbf{D} - \Phi \frac{\partial F}{\partial \mathbf{n}} \cdot \mathbf{N} - (1-\Phi) \frac{\partial F}{\partial \mathbf{m}} \cdot \mathbf{M} \tag{4}$$

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 [18] of the directors $\mathbf{N}$ and $\mathbf{M}$, given by

$$N_i = \dot{n}_i - W_{ij} n_j; \quad M_i = \dot{m}_i - W_{ij} m_j; \quad W_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right) \tag{5 a, b, c}$$

where $\mathbf{v}$ is the velocity vector, $\mathbf{W}$ is the antisymmetric vorticity tensor, and the superposed dot denotes material differentiation. The constraints $\mathbf{n} \cdot \mathbf{N} = 0$ and $\mathbf{M} \cdot \mathbf{M} = 0$ arise due to the unit length constraint on the directors ($\mathbf{n} \cdot \mathbf{n} = 1$, $\mathbf{m} \cdot \mathbf{m} = 1$). The forces appearing in equation (4) are the symmetric traceless rate of deformation tensor $\mathbf{D}$, and the two vector molecular fields $-\partial F/\partial \mathbf{n}$ and $-\partial F/\partial \mathbf{m}$, given by

$$D_{ij} = \frac{1}{2}\left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right] \tag{6 a}$$

and

$$\begin{aligned} -\frac{\partial F}{\partial n_i} &= -\kappa(\mathbf{n} \cdot \mathbf{m})[m_i - (\mathbf{n} \cdot \mathbf{m}) n_i]; \\ -\frac{\partial F}{\partial m_i} &= -\kappa(\mathbf{n} \cdot \mathbf{m})[n_i - (\mathbf{n} \cdot \mathbf{m}) m_i] \end{aligned} \tag{6 b}$$

where the unit length restriction on the directors $\mathbf{n}$ and $\mathbf{m}$ has been incorporated. A linear expansion of the fluxes $\{\mathbf{t}^s, \Phi\mathbf{N}, (1-\Phi)\mathbf{M}\}$ in terms of the forces $\{\mathbf{D}, -\partial F/\partial \mathbf{n}, -\partial F/\partial \mathbf{m}\}$ gives

$$\begin{bmatrix} \mathbf{t}^s \\ \Phi\mathbf{N} \\ (1-\Phi)\mathbf{M} \end{bmatrix} = \begin{bmatrix} \mathbf{L}^{11} & -\mathbf{L}^{12^T} & -\mathbf{L}^{13^T} \\ \mathbf{L}^{12} & \mathbf{L}^{22} & \mathbf{L}^{23^T} \\ \mathbf{L}^{13} & \mathbf{L}^{23} & \mathbf{L}^{33} \end{bmatrix} \begin{bmatrix} \mathbf{D} \\ -\dfrac{\partial F}{\partial \mathbf{n}} \\ -\dfrac{\partial F}{\partial \mathbf{m}} \end{bmatrix} \tag{7}$$

where T denotes transpose, and where the symmetry of the coefficient matrix follows from Onsager reciprocal relations [19]. The minus signs in the first row of the matrix of coefficients arises because $\mathbf{D}$ is odd with respect to time inversion but both $-\partial F/\partial \mathbf{n}$ and $\partial F/\partial \mathbf{m}$ are even. Assuming that the tensor coefficients are dependent on Φ, $\mathbf{n}$ and $\mathbf{m}$, taking into account the tensor order of the forces and fluxes, and the possible sign reversals of the fluxes with reversals in $\mathbf{n}$ and $\mathbf{m}$ we obtain

$$t_{ij} = L^{11}_{ijkl} D_{lk} + L^{12}_{kij} \frac{\partial F}{\partial n_k} + L^{13}_{kij} \frac{\partial F}{\partial m_k}, \tag{8 a}$$

$$\Phi N_i = L^{12}_{ijk} D_{kj} - L^{22}_{ij} \frac{\partial F}{\partial n_j} - L^{23}_{ji} \frac{\partial F}{\partial m_j}, \tag{8 b}$$

and

$$(1-\Phi)M_i = L^{13}_{ijk}D_{kj} - L^{23}_{ij}\frac{\partial F}{\partial n_j} - L^{33}_{ij}\frac{\partial F}{\partial m_j} \qquad (8\,c)$$

where the expressions for the coefficients are listed in the Appendix. The coefficients appearing in $\mathbf{L}^{11}$ have viscosity units, the coefficients appearing in $\mathbf{L}^{22}$, $\mathbf{L}^{33}$, and $\mathbf{L}^{23}$ have units of reciprocal viscosity, and those appearing in $\mathbf{L}^{12}$ and $\mathbf{L}^{13}$ are dimensionless parameters, commonly known as reactive parameters [3].

As shown in the Appendix the two governing director equations are given by

$$\Phi\mathbf{N} = \Phi\lambda^{\mathrm{n}}[\mathbf{D}\cdot\mathbf{n} - (\mathbf{D}:\mathbf{nn})\mathbf{n}] + \Phi(1-\Phi)\left[\Lambda^{\mathrm{nm}}(\mathbf{D}:\mathbf{nm}) - \frac{\kappa}{\gamma_1^{\mathrm{n}}}(\mathbf{n}\cdot\mathbf{m})\right][\mathbf{m}-(\mathbf{n}\cdot\mathbf{m})\mathbf{n}] \qquad (9\,a)$$

$$(1-\Phi)\mathbf{M} = (1-\Phi)\lambda^{\mathrm{m}}[\mathbf{D}\cdot\mathbf{m} - (\mathbf{D}:\mathbf{mm})\mathbf{m}] + \Phi(1-\Phi)\left[\Lambda^{\mathrm{mn}}(\mathbf{D}:\mathbf{nm}) - \frac{\kappa}{\gamma_1^{\mathrm{m}}}(\mathbf{n}\cdot\mathbf{m})\right][\mathbf{n}-(\mathbf{n}\cdot\mathbf{m})\mathbf{m}]$$

where 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 $\mathbf{n}$ and $\mathbf{m}$, respectively; these six parameters are temperature and concentration dependent. The ratios $\gamma_1^{\mathrm{n}}/|\kappa|$ and $\gamma_1^{\mathrm{m}}/|\kappa|$ are the two director relaxation times of the model. Expressions for the symmetric and antisymmetric contributions to the viscous extra stress tensor are given and discussed in the Appendix. Here and in the rest of the paper we restrict the analysis to alignment behaviour, and therefore consider the two director equations (9 *a*, *b*) in detail.

Equations (9) show that this model predicts that the flow-orienting properties will depend on the signs and magnitudes of the four reactive parameters $(\lambda^{\mathrm{n}}, \lambda^{\mathrm{m}}, \Lambda^{\mathrm{nm}}, \Lambda^{\mathrm{mn}})$. As is well known [3], thermodynamic restrictions do not restrict the signs of these four reactive parameters, 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 [18] and, as shown below, 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 (biaxiality) if $\kappa<0$ ($\kappa>0$). Dotting equation (9 *a*) with $\mathbf{n}$ yields $\mathbf{N}\cdot\mathbf{n}=0$, and dotting (9 *b*) with $\mathbf{m}$ yields $\mathbf{M}\cdot\mathbf{m}=0$, as required. In addition equations (9) show that $\mathbf{N}(\mathbf{n}) = -\mathbf{N}(-\mathbf{n})$ and $\mathbf{M}(\mathbf{m}) = -\mathbf{M}(-\mathbf{m})$, as required.

An important observation regarding equations (9) is that the presence of the elastic terms in the director equations, provide for a mechanism that introduces dependence of the stationary director orientation on the rate of deformation. For example, for shear flow-alignment the model predicts that the director angles are a function of the shear rate, a feature that is present in nematic polymers [20] but it is not captured by the Leslie–Ericksen theory [3] for uniaxial nematics or by director theories for orthorhombic biaxial nematics [11–13]. This mechanism was first identified in [11] for binary nematic mixtures that are biaxial at rest.

An important observation regarding the consistency equations (9) is that they properly reduce to the governing director equations for spatially uniform orthorhombic biaxial nematic liquid crystals, as seen by imposing the biaxiality constraint $\mathbf{n}\cdot\mathbf{m}=0$ in equations (9):

$$\mathbf{N} = \lambda^{\mathrm{n}}[\mathbf{D}\cdot\mathbf{n} - (\mathbf{D}:\mathbf{nn})\mathbf{n}] + \bar{\Lambda}^{\mathrm{nm}}[(\mathbf{D}:\mathbf{nm})\mathbf{m}] \qquad (10\,a)$$

and

$$\mathbf{M} = \lambda^{\mathrm{m}}[\mathbf{D}\cdot\mathbf{m} - (\mathbf{D}:\mathbf{mm})\mathbf{m}] + \bar{\Lambda}^{\mathrm{mn}}[(\mathbf{D}:\mathbf{nm})\mathbf{n}] \qquad (10\,b)$$

where $\bar{\Lambda}^{\mathrm{nm}} = (1-\Phi)\Lambda^{\mathrm{nm}}$ and $\bar{\Lambda}^{\mathrm{mn}} = (1-\Phi)\Lambda^{\mathrm{mn}}$.

By setting $\Phi=1$ in equations (9 *a*, *b*), it is straightforward to show that the director model properly reduces to the well-known viscous TIF model [18] applicable to single component low molar mass nematics, and containing a single reactive parameter $\lambda^{\mathrm{n}} = \lambda = -\gamma_2/\gamma_1$. In the TIF model shear flow-alignment of rod-like (disc-like) nematics exists if $\lambda>1$ ($\lambda<-1$), and non-alignment if $0<\lambda<1$ ($0>\lambda>-1$). In the alignment regime of rod-like (disc-like) nematics, the director lies in the shear plane and is oriented with the positive (modulo $\pm\pi$) Leslie angle θ_{L} with respect to the flow direction, which given by

$$\theta_{\mathrm{L}} = \frac{1}{2}\cos^{-1}\frac{1}{\lambda}; \quad \begin{cases}\text{Rods: } 0 \leqslant \theta_{\mathrm{L}} \leqslant \pi/4\\ \text{Discs: } \pi/2 \leqslant \theta_{\mathrm{L}} \leqslant 3\pi/4\end{cases} \qquad (11)$$

where positive angles are measured anti-clockwise.

Below we present the predictions of the theory (equations (9)), and restrict the analysis to slow flow regimes, which is defined by

$$\frac{\|\nabla v\|\,\max(\gamma_1)}{|\kappa|} \ll 1 \qquad (12)$$

where the double bars denotes the norm and $\max(\gamma_1)$ denotes the maximum rotational viscosity of the two components (γ_1, γ_2). If equation (12) holds uniaxial (biaxial) mixtures at rest remain uniaxial (biaxial) when subjected to sufficiently weak flows. Results for the non-linear strong flow regime, where effects of the magnitude of the shear rate dictates alignment behaviour [11, 14] is beyond the scope of this paper.

3. Uniaxial mixtures in slow flows

Here we consider the rheology and flow-alignment of single-phase uniaxial nematic mixtures consisting of binary rod–rod and disc–disc solutions. In the presence of slow flows uniaxiality is retained, since the elastic restoring mechanism is sufficiently stronger that flow-induced biaxiality. Thus we consider the case where **n** = **m**, and **N** = **M**. In this case equations (9) collapse into the following single equation:

$$\gamma_1^{\mathrm{mix}}\mathbf{N} = \lambda_{\mathrm{o}}^{\mathrm{mix}}\gamma_1^{\mathrm{mix}}[\mathbf{D}\cdot\mathbf{n} - (\mathbf{D}:\mathbf{nn})\mathbf{n}] \tag{13}$$

where the mixture's rotational viscosity γ_1^{mix} and reactive parameter $\lambda_{\mathrm{o}}^{\mathrm{mix}}$ in the slow flow limit are given by

$$\gamma_1^{\mathrm{mix}} = \Phi\gamma_1^{\mathrm{n}} + (1-\Phi)\gamma_1^{\mathrm{m}} \tag{14a}$$

and

$$\lambda_{\mathrm{o}}^{\mathrm{mix}} = \frac{\Phi R}{\Phi(R-1)+1}\lambda^{\mathrm{n}} + \frac{(1-\Phi)}{\Phi(R-1)+1}\lambda^{\mathrm{m}}; \quad R(\Phi) = \frac{\gamma_1^{\mathrm{n}}}{\gamma_1^{\mathrm{m}}} \tag{14b}$$

where $R(\Phi)$ is the ratio of the rotational viscosities of the two components, and where the subscript 'o' in $\lambda_{\mathrm{o}}^{\mathrm{mix}}$ indicates slow flow regime.

3.1. *Rotational viscosity mixture rule*

The rotational viscosity for the nematic mixture γ^{mix} is given in equation (14*a*), and it follows a non-linear mixture rule, since as shown in the Appendix, the rotational viscosities of the components $(\gamma_1^{\mathrm{n}}, \gamma_1^{\mathrm{m}})$ depend on concentration. Using equations (A 15*c*, A 17*c*) in equation (14*a*) gives the following expression for the mixture rotational viscosity:

$$\gamma_1^{\mathrm{mix}} = \frac{\Phi}{(\alpha_1^{22}+\alpha_3^{22}) + \alpha_1^{23}\Phi(1-\Phi)} + \frac{(1-\Phi)}{(\alpha_1^{33}+\alpha_2^{33}) + \alpha_1^{23}\Phi(1-\Phi)}. \tag{15}$$

To capture trends we introduce the scaled mixture rotational viscosity $\tilde{\gamma}_1^{\mathrm{mix}} = \gamma_1^{\mathrm{mix}}/\gamma_1^{\mathrm{m}}(\Phi=0)$. Figure 1 shows the scaled mixture rotational viscosity as a function of the volume fraction Φ; parameters: $(\alpha_1^{22}+\alpha_3^{22})/\gamma_1^{\mathrm{m}}(0) = 1{\cdot}5$, $\alpha_1^{23}/\gamma_1^{\mathrm{m}}(0) = 3$, $(\alpha_1^{33}+\alpha_2^{33})/\gamma_1^{\mathrm{m}}(0) = 1$. This type of concentration dependence of the rotational viscosity is shown in actual binary mixtures of polar azoxy rod-like nematics [15].

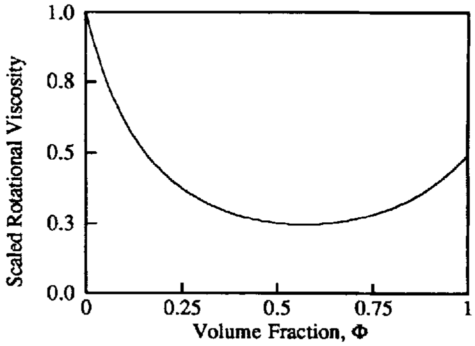

Figure 1. Scaled mixture rotational viscosity $\gamma_1^{\mathrm{mix}}/\gamma_1^{\mathrm{m}}(0)$ as a function of the volume fraction Φ, according to equation (15). Parameters: $(\alpha_1^{22}+\alpha_3^{22})/\gamma_1^{\mathrm{m}}(0) = 1{\cdot}5$, $\alpha_1^{23}/\gamma_1^{\mathrm{m}}(0) = 3$, $(\alpha_1^{33}+\alpha_2^{33})/\gamma_1^{\mathrm{m}}(0) = 1$. This type of concentration dependence of the rotational viscosity is shown in actual binary mixtures of polar azoxy rod-like nematics [15].

3.2. *Flow-alignment mixture rule*

Specific predictions for rod–rod and disc–disc mixtures are shown in the following sections, but general results for uniaxial mixtures are discussed in this section. According to equation (13) the shear flow-alignment properties of a binary uniaxial mixture (i.e. slow flow) are given by the mixture reactive parameter $\lambda_{\mathrm{o}}^{\mathrm{mix}}$, shown in equation (14*b*). An important observation is that for the slow flow regime of uniaxial mixtures, dynamic interaction parameters play no role. The Leslie alignment angle of the mixture $\theta_{\mathrm{L}}^{\mathrm{mix}}$ is now given by

$$\theta_{\mathrm{L}}^{\mathrm{mix}} = \frac{1}{2}\cos^{-1}\left(\frac{1}{\lambda_{\mathrm{o}}^{\mathrm{mix}}}\right); \quad \begin{cases} \text{rods: } 0 \leqslant \theta_{\mathrm{L}} \leqslant \pi/4 \\ \text{discs: } \pi/2 \leqslant \theta_{\mathrm{L}} \leqslant 3\pi/4. \end{cases} \tag{16}$$

The mixture reactive parameter $\lambda_{\mathrm{o}}^{\mathrm{mix}}$ depends on the concentration Φ, the ratio of component rotational viscosities R, and the single component reactive parameters λ^{n} and λ^{m}. When $R = 1$ the alignment mixture rule simplifies to

$$\lambda_{\mathrm{o}}^{\mathrm{mix}} = \Phi\lambda^{\mathrm{n}} + (1-\Phi)\lambda^{\mathrm{m}} \tag{17}$$

which is the simplest mixture rule, and which may only be observed with components of approximately equal molecular weights. On the other hand, for monomer–polymer mixtures $R \to 0$, and the mixture reactive parameter is approximated by the reactive parameter of the polymer:

$$\lambda_{\mathrm{o}}^{\mathrm{mix}} = \lambda^{\mathrm{m}}. \tag{18}$$

In this case if the polymer is non-aligning (aligning) at slow flows the mixture is non-aligning (aligning).

3.3. *Flow-alignment rules for uniaxial mixtures of rod-like nematics*

In this section **n** and **m** represent the directors of the two rod-like nematic components of the uniaxial nematic mixture. For rod-like nematics the component reactive parameters are positive: $\lambda^n > 0$ and $\lambda^m > 0$. According to equation (14*b*) the mixture reactive parameter λ_o^{mix} is a function of R, Φ, λ^n, and λ^m.

Figure 2 shows the mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ for two aligning components (top of figure 2), a mixture of aligning–non-aligning components (middle of figure 2), and a mixture of two non-aligning components (bottom of figure 2); for R : 100 (full line), 1 (dashed-dot line), and 0·1 (dashed-triple dot line). The figure show that alignment transitions ($@\,\lambda_o^{mix} = +1$) are only predicted for mixtures of aligning–non-aligning (middle figure) components. The other two cases, mixtures of two aligning components (top figure), and mixtures of two non-aligning components (bottom figure) show no crossover. The figure also shows the effect of $R = \gamma_1^n/\gamma_1^m$ on λ_o^{mix}; large (small) R results in $\lambda_o^{mix} \approx \lambda^n$ ($\lambda_o^{mix} \approx \lambda^m$) for $\Phi > 0$ ($1 - \Phi > 0$).

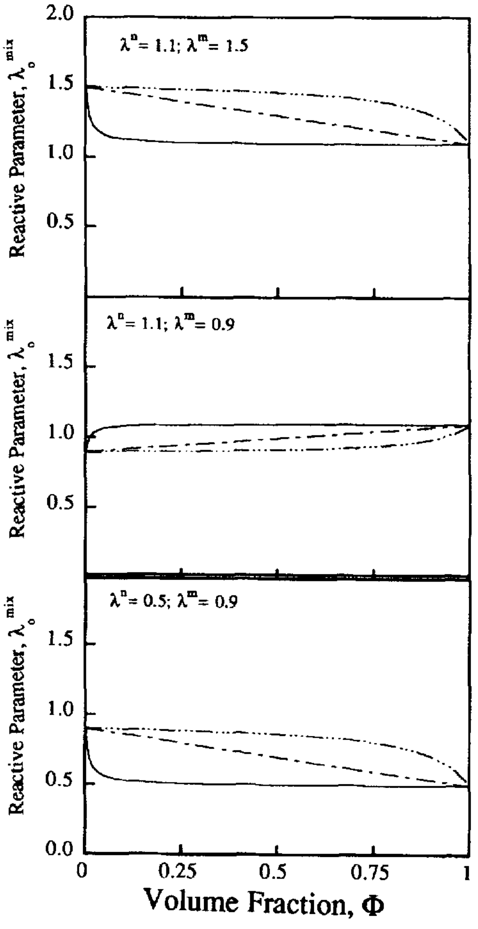

Figure 2. Uniaxial rod–rod mixtures. Mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ for two rod-like aligning (top figure), a mixture of aligning–non-aligning rod-like components (middle figure), and a mixture of two non-aligning rod-like components (bottom figure); and R: 100 (full line), 1 (dashed-dot line), and 0·1 (dashed-triple dot line). Alignment transitions are only predicted for mixtures of aligning–non-aligning components (middle figure).

The alignment transition ($@\,\lambda_o^{mix} = +1$) predicted for mixtures of aligning and non-aligning rod-like nematic components (middle plot of figure 2) occurs at

$$R = \frac{\gamma_1^n}{\gamma_1^m} = \frac{(1-\Phi)(1-\lambda^m)}{\Phi(\lambda^n - 1)}; \quad \lambda^n > 1; \quad 0 < \lambda^m < 1. \tag{19}$$

Figure 3 shows the viscosity ratio $R = \gamma_1^n/\gamma_1^m$ as a function of the volume fraction Φ for $\lambda^n = 1{\cdot}1$ and λ^m : 0·9 (full line), 0·5 (dashed-dot line), and 0·01 (dashed-triple dot line). The lines in the figure indicate the alignment transition for a given (R, Φ). For a given R, smaller (larger) λ^m results in transitions at higher (lower) Φ. For a given Φ, smaller (larger) λ^m results in transitions at higher (lower) R. For a given set of reactive parameters the region above (below) each line corresponds to alignment (non-alignment).

3.4. *Flow-alignment rules for uniaxial mixtures of disc-like nematics*

In this section **n** and **m** represent the directors of the two disc-like nematic components of the uniaxial nematic mixture. For disc-like nematics the component reactive parameters are negative: $\lambda^n < 0$ and $\lambda^m < 0$. According to equation (27) the mixture reactive parameter λ_o^{mix} is a function of R, Φ, λ^n, and λ^m. To simplify the analysis in this section we neglect the concentration dependence in R.

Figure 4 shows the mixture reactive parameter λ_o^{mix} as

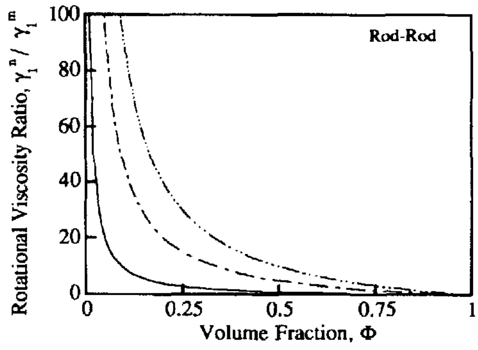

Figure 3. Uniaxial rod–rod mixtures. Rotational viscosity ratio $R = \gamma_1^n/\gamma_1^m$ as a function of the volume fraction Φ for $\lambda^n = 1{\cdot}1$ and λ^m: 0·9 (full line), 0·5 (dashed-dot line), and 0·01 (dashed-triple dot line), for mixtures of two rod-like nematics. The lines in the figure indicate the alignment transition ($\lambda_o^{mix} = 1$) for a given (R, Φ). The volume fraction Φ corresponds to the component with director **n**.

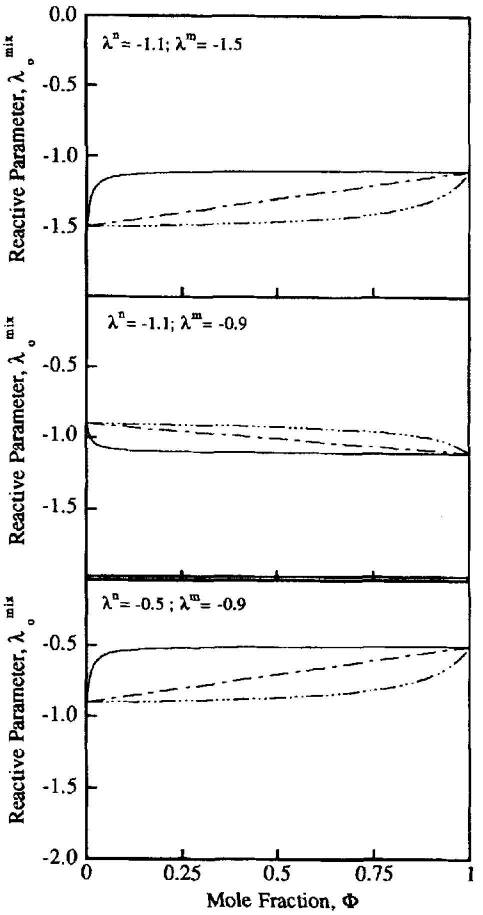

Figure 4. Uniaxial disc–disc mixtures. Mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ for two aligning disc-like components (top figure), a mixture of aligning–non-aligning disc-like components (middle figure), and a mixture of two non-aligning disc-like components (bottom figure); and R: 100 (full line), 1 (dashed-dot line), and 0·1 (dashed-triple dot line). Alignment transitions for mixtures of aligning–non-aligning (middle figure) disc-like components.

a function of the volume fraction Φ for two aligning components (top), a mixture of aligning–non-aligning components (middle), and a mixture of two non-aligning components (bottom); for R: 100 (full line), 1 (dashed-dot line), and 0·1 (dashed-triple dot line). The figure shows that alignment transitions ($@\,\lambda_o^{mix} = -1$) are only predicted for mixtures of aligning–non-aligning (middle figure) components. The other two cases (top and bottom figures) show no crossover. The figure also shows the effect of $R = \gamma_1^n/\gamma_1^m$ on λ_o^{mix}; large (small) R results in $\lambda_o^{mix} \approx \lambda^n$ ($\lambda_o^{mix} \approx \lambda^m$) for $\Phi > 0$ $(1-\Phi > 0)$.

The alignment transition ($@\,\lambda_o^{mix} = -1$) observed in mixtures of aligning and non-aligning discotic nematic components (middle plot of figure 4) occurs at

$$R = \frac{\gamma_1^n}{\gamma_1^m} = \frac{(1-\Phi)(-1-\lambda^m)}{\Phi(1+\lambda^n)}; \quad \lambda^n < -1; \quad -1 < \lambda^m < 0. \tag{20}$$

Figure 5 shows the viscosity ratio $R = \gamma_1^n/\gamma_1^m$ as a function of the volume fraction Φ for $\lambda^n = -1{\cdot}1$ and $\lambda^m = -0{\cdot}9$ (full line), $-0{\cdot}5$ (dashed-dot line), and $-0{\cdot}01$ (dashed-triple dot line). The lines in the figure indicate the alignment transition for a given (R, Φ). For a given R, larger (smaller) λ^m results in transitions at higher (lower) Φ. For a given Φ, larger (smaller) λ^m results in transitions at higher (lower) R. For a given set of reactive parameters the region above (below) each line corresponds to alignment (non-alignment).

4. Biaxial mixtures in slow flows

Here we consider the rheology and flow-alignment of single-phase biaxial nematic mixtures consisting of binary rod–disc solutions. In the presence of slow flows biaxiality is retained, since the elastic restoring mechanism is sufficiently stronger than flow-induced biaxiality. Thus we consider the case where $\mathbf{n}\cdot\mathbf{m} = 0$, where $\mathbf{n}(\mathbf{m})$ refers to the rod-like (disc-like) component. In this case equations (9) simplify to

$$\Phi\gamma_1^n\mathbf{N} = \Phi\gamma_1^n\lambda^n[\mathbf{D}\cdot\mathbf{n} - (\mathbf{D}:\mathbf{nn})\mathbf{n}] + \Phi(1-\Phi)\gamma_1^n\Lambda^{nm}(\mathbf{D}:\mathbf{nm})\mathbf{m} \tag{21a}$$

and

$$(1-\Phi)\gamma_1^m\mathbf{M} = (1-\Phi)\gamma_1^m\lambda^m[\mathbf{D}\cdot\mathbf{m} - (\mathbf{D}:\mathbf{mm})\mathbf{m}] + \Phi(1-\Phi)\gamma_1^m\Lambda^{mn}(\mathbf{D}:\mathbf{nm})\mathbf{n}. \tag{21b}$$

To make further progress we now consider flow-alignment in rectilinear shear flow.

Assuming a known incompressible rectilinear simple shear flow, with velocity components in rectangular

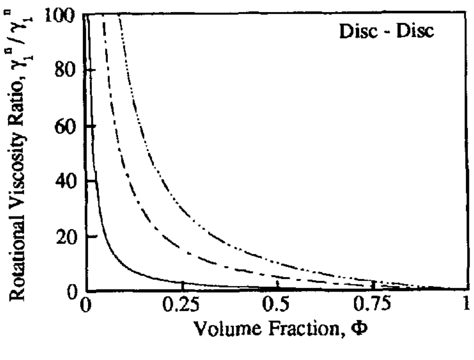

Figure 5. Uniaxial disc–disc mixtures. Rotational viscosity ratio $R = \gamma_1^n/\gamma_1^m$ as a function of the volume fraction Φ for $\lambda^n = 1{\cdot}1$ and λ^m: $-0{\cdot}9$ (full line), $-0{\cdot}5$ (dashed-dot line), and $-0{\cdot}01$ (dashed-triple dot line) for mixtures of two disc-like nematics. The lines in the figure indicate the alignment transition ($\lambda_o^{mix} = -1$) for a given (R, Φ).

coordinates given by $\mathbf{v}=(v_x,v_y,v_z)=(\dot{\gamma}y,0,0)$, the non-zero components of the rate of deformation tensor $\mathbf{D}$ and vorticity tensor $\mathbf{W}$ are

$$D_{xy}=D_{yx}=\dot{\gamma}/2;\quad W_{xy}=-W_{yx}=\dot{\gamma}/2 \qquad (22\,a,b)$$

where $\dot{\gamma}$ is the shear rate ($\dot{\gamma}\geqslant 0$), x is the flow direction, the x–y plane is the shear plane, and z is along the vorticity direction. The two director fields are parametrized as follows:

$$\begin{aligned}\mathbf{n}&=(n_x,n_y,n_z)=(\cos\theta_1,\sin\theta_1,0)\\ \mathbf{m}&=(m_x,m_y,m_z)=(\cos\theta_2,\sin\theta_2,0)\end{aligned} \qquad (23\,a,b)$$

where positive angles are measured anti-clockwise. Replacing (22) and (23) into the governing equations (9) we obtain, after scaling, the following dimensionless governing equations for θ_1 and θ_2:

$$\begin{aligned}\dot{\theta}_1 =& -P[1-\lambda^{\mathrm{n}}\cos 2\theta_1]\\ &-[P\Lambda^{\mathrm{nm}}\sin(\theta_1+\theta_2)-\cos(\theta_1-\theta_2)]\\ &\times[\cos\theta_2-\cos(\theta_1-\theta_2)\cos\theta_2]/\sin\theta_1 \qquad (24\,a)\end{aligned}$$

$$\begin{aligned}\dot{\theta}_2 =& -P[1-\lambda^{\mathrm{m}}\cos 2\theta_2]\\ &-[P\Lambda^{\mathrm{mn}}\sin(\theta_2+\theta_1)-R\cos(\theta_2-\theta_1)]\\ &\times[\cos\theta_1+\cos(\theta_2-\theta_1)\cos\theta_1]/\sin\theta_2 \qquad (24\,b)\end{aligned}$$

where the dimensionless parameter is given by

$$P=\frac{\dot{\gamma}\gamma_1^{\mathrm{n}}}{2|\kappa|} \qquad (25)$$

and where the time is now scaled with $|\kappa|/\gamma_1^{\mathrm{n}}$. The director angle of the rods (θ_1) and of the discs (θ_2) are restricted by the biaxiality condition: $\theta_2=\theta_1+\pi/2$. A steady state biaxial solution to equations (16) is given by

$$\cos(2\theta_{1,\mathrm{L}})=\frac{R\Phi+(1-\Phi)}{R\Phi\lambda^{\mathrm{n}}-(1-\Phi)\lambda^{\mathrm{m}}+\Phi(1-\Phi)[R\Lambda^{\mathrm{nm}}-\Lambda^{\mathrm{mn}}]};$$

$$\theta_{2,\mathrm{L}}=\theta_{1,\mathrm{L}}+\pi/2 \qquad (26\,a,b)$$

where the subscript denotes the Leslie angle. From equations (26) it follows that the mixture's rotational viscosity γ_1^{mix} and reactive parameter $\lambda_{\mathrm{o}}^{\mathrm{n,mix}}$ of the rod-like component ($\mathbf{n}$) in the slow flow limit are given by

$$\gamma_1^{\mathrm{mix}}=\Phi\gamma_1^{\mathrm{n}}+(1-\Phi)\gamma_1^{\mathrm{m}} \qquad (27\,a)$$

and

$$\lambda_{\mathrm{o}}^{\mathrm{n,mix}}=\frac{\Phi R}{\Phi(R-1)+1}\lambda^{\mathrm{n}}+\frac{(1-\Phi)}{\Phi(R-1)+1}\lambda^{\mathrm{m}}-\frac{\Phi(1-\Phi)}{\Phi(R-1)+1}[R\Lambda^{\mathrm{nm}}-\Lambda^{\mathrm{mn}}]. \qquad (27\,b)$$

Since the rod–disc mixture is biaxial ($\mathbf{n}\cdot\mathbf{m}=0$) it is useful to introduce the following reactive parameters:

$$\lambda_{\mathrm{o}}^{\mathrm{mix}}=\lambda_{\mathrm{o}}^{\mathrm{n,mix}}=-\lambda_{\mathrm{o}}^{\mathrm{m,mix}} \qquad (28)$$

where is $\lambda_{\mathrm{o}}^{\mathrm{mix}}$ denoted as the mixture's reactive parameter. The biaxial mixture is of the shear flow-aligning type if $\lambda_{\mathrm{o}}^{\mathrm{mix}}>1$, and of the non-aligning type if $0<\lambda_{\mathrm{o}}^{\mathrm{mix}}<1$. For aligning mixtures the directors align in the shear plane, as follows:

$$\begin{aligned}&\theta_{1,\mathrm{L}}=\frac{1}{2}\cos^{-1}\left(\frac{1}{\lambda_{\mathrm{o}}^{\mathrm{mix}}}\right);\quad 0\leqslant\theta_{1,\mathrm{L}}\leqslant\pi/4,\\ &\pi/2\leqslant\theta_{2,\mathrm{L}}\leqslant 3\pi/4,\quad \theta_{2,\mathrm{L}}=\theta_{1,\mathrm{L}}+\pi/2.\end{aligned} \qquad (29)$$

The mixture's rotational viscosity γ_1^{mix} for in-plane motion is given by the simple law of mixtures, as for uniaxial mixtures (see equation (15)) and similar conclusions can be drawn for the present case. On the other hand the mixture reactive parameter now contains the dynamic interaction terms $[R\Lambda^{\mathrm{nm}}-\Lambda^{\mathrm{mn}}]$, not present in uniaxial mixtures (see equation (14 *b*)). The alignment mixture rule for biaxial mixtures is thus characterized by a non-linear concentration factor introducing each reactive parameter, and by a non-linear concentration factor introducing an interaction term. The effect of molecular weight asymmetry is captured by the magnitude of $R=\gamma_1^{\mathrm{n}}/\gamma_1^{\mathrm{m}}$, and two limiting cases arise: (i) *Mixtures of polymeric rods–monomeric discs*: in this case $R\gg 1$, and the mixture's reactive parameter simplifies to

$$\lambda_{\mathrm{o}}^{\mathrm{mix}}=\lambda^{\mathrm{n}}+(1-\Phi)\Lambda^{\mathrm{nm}} \qquad (30)$$

and the alignment properties of the solution are dictated by the rod-like component and a concentration dependent factor containing one interaction parameter. (ii) *Mixtures of polymeric discs–monomeric rods*: in this case $R\ll 1$, and the mixture's reactive parameter simplifies to

$$\lambda_{\mathrm{o}}^{\mathrm{mix}}=-\lambda^{\mathrm{m}}-\Phi\Lambda^{\mathrm{mn}} \qquad (31)$$

and the alignment properties of the solution are dictated by the disc-like component and a concentration dependent factor containing one interaction parameter.

4.1. *Flow-alignment rules for biaxial mixtures of disc-like and rod-like nematics*

Recall that for rod-like nematics the component reactive parameters is positive $\lambda^{\mathrm{n}}>0$, and for disc-like nematics is negative $\lambda^{\mathrm{m}}<0$. According to equations (27 *b*, 28) the mixture reactive parameter $\lambda_{\mathrm{o}}^{\mathrm{mix}}$ is a function of R, Φ, λ^{n}, and λ^{m}, Λ^{nm} and Λ^{mn}. To simplify the analysis we neglect the concentration dependence in R. According to the type of dynamic interactions (sign and magnitude of A^{nm} and A^{mn}) we may have no dynamic interaction, positive dynamic interactions, and negative dynamic interaction.

4.1.1. *Mixtures with no dynamic interaction*

In this case $A^{nm} = A^{mn} = 0$, and the reactive parameter λ_o^{mix} simplifies to

$$\lambda_o^{mix} = \frac{\Phi R}{\Phi(R-1)+1}\lambda^n - \frac{(1-\Phi)}{\Phi(R-1)+1}\lambda^m \qquad (32)$$

which is identical to the uniaxial case (see equation (14*b*)).

Figure 6 shows the mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ; top figure: two aligning components ($\lambda^n = -\lambda^m = 1{\cdot}1$); middle figure: a mixture of non-aligning rods ($\lambda^n = 0{\cdot}9$) with aligning discs ($\lambda^m = -1{\cdot}1$); bottom figure: mixture of aligning rods ($\lambda^n = 1{\cdot}1$) with non-aligning discs ($\lambda^m = -0{\cdot}9$); R: 0·1 (full line), 1 (dashed-dot line), and 10 (dashed-triple dot line). The figure shows that alignment transitions (@ $\lambda_o^{mix} = +1$) are predicted for mixtures of aligning–non-aligning (middle and bottom figure) components. The other case (top figure) show no crossover. The figure also shows the effect of $R = \gamma_1^n/\gamma_1^m$ on λ_o^{mix}; large (small) R results in $\lambda_o^{mix} \approx \lambda^n$ ($\lambda_o^{mix} \approx -\lambda^m$) for $\Phi > 0$ ($1-\Phi > 0$).

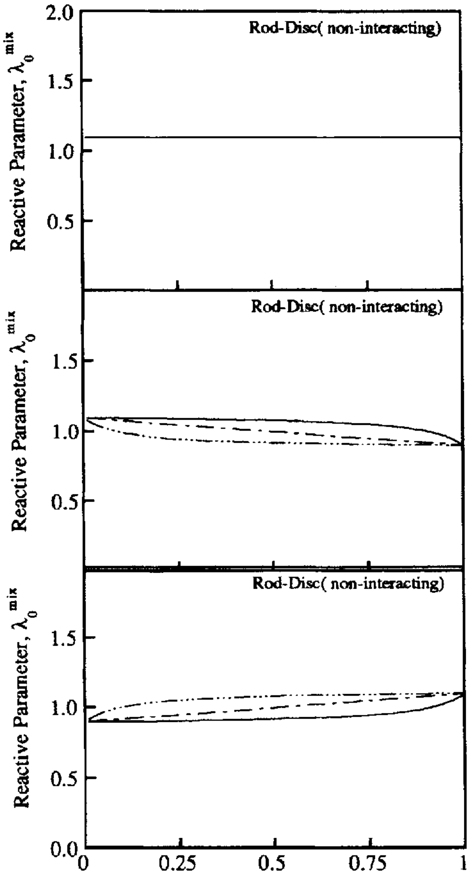

Figure 6. Biaxial rod–disc mixtures with no dynamic coupling. Mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ; top figure: two aligning components ($\lambda^n = -\lambda^m = 1{\cdot}1$); middle figure: a mixture of non-aligning rods ($\lambda^n = 0{\cdot}9$) with aligning discs ($\lambda^m = -1{\cdot}1$); bottom figure: mixture of aligning rods ($\lambda^n = 1{\cdot}1$) with non-aligning discs ($\lambda^m = -0{\cdot}9$); R: 0·1 (full line), 1 (dashed-dot line), and 10 (dashed-triple dot line). Alignment transitions are predicted for mixtures of aligning–non-aligning (middle and bottom figure) components.

The alignment transition (@ $\lambda_o^{mix} = +1$) observed in mixtures of aligning rods (discs) and non-aligning discs (rods) occurs at

$$R = \frac{\gamma_1^n}{\gamma_1^m} = \frac{(1-\Phi)(-1-\lambda^m)}{\Phi(1-\lambda^n)}. \qquad (33)$$

Figure 7 shows the viscosity ratio $R = \gamma_1^n/\gamma_1^m$ at which the alignment transition occurs as a function of the volume fraction Φ for $\lambda^n = 0{\cdot}9$ and $\lambda^m = -1{\cdot}1$. The opposite case $\lambda^n = 1{\cdot}1$ and $\lambda^m = -0{\cdot}9$ gives the same line. The line in the figure indicates the alignment transition for a given (R, Φ). Addition of non-aligning rods (discs) to aligning discs (rods) eventually leads to non-alignment.

4.1.2. *Mixtures with positive dynamic interaction*

In this case $A^{nm} > 0$, $A^{mn} < 0$. To simplify the analysis we assume $A^{nm} = \lambda^n > 0$, $A^{mn} = \lambda^m < 0$. The mixture's reactive parameter λ_o^{mix} simplifies to

$$\lambda_o^{mix} = \frac{\Phi R + \Phi(1-\Phi)R}{\Phi(R-1)+1}\lambda^n - \frac{(1-\Phi)+\Phi(1-\Phi)}{\Phi(R-1)+1}\lambda^m. \qquad (34)$$

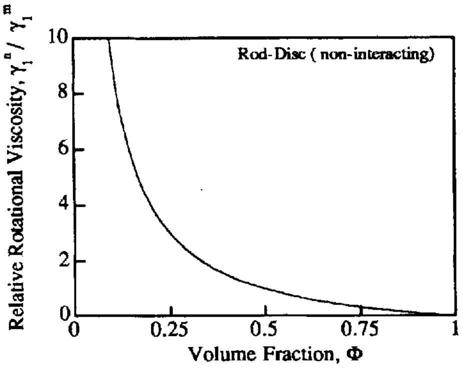

Figure 7. Biaxial rod–disc mixtures with no dynamic coupling. Viscosity ratio $R = \gamma_1^n/\gamma_1^m$ as a function of the volume fraction Φ for $\lambda^n = 0{\cdot}9$ and λ^m: $-1{\cdot}1$. The opposite case $\lambda^n = 1{\cdot}1$ and λ^m: $-0{\cdot}9$ gives the same line. The line in the figure indicates the alignment transition ($\lambda_o^{mix} = \lambda_o^{n,mix} = 1$, $\lambda_o^{m,mix} = -1$) for a given (R, Φ). Addition of non-aligning rods (discs) to aligning discs (rods) eventually leads to non-alignment.

Figure 8 shows the mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ; top figure: two aligning components ($\lambda^n = -\lambda^m = 1{\cdot}1$); middle figure: a mixture of non-aligning rods ($\lambda^n = 0{\cdot}9$) with aligning discs ($\lambda^m = -1{\cdot}1$); bottom figure: mixture of aligning rods ($\lambda^n = 1{\cdot}1$) with non-aligning discs ($\lambda^m = -0{\cdot}9$); R: 0·1 (full line), 1 (dashed-dot line), and 10 (dashed-triple dot line). The figure show alignment transitions, that is λ_o^{mix} crosses the value of 1 are predicted for mixtures of aligning–non-aligning (middle and bottom figure) components. The other case (top figure) show no crossover. The figure shows that positive interactions promote alignment. The degree of asymmetry of the profiles increases when R deviates from unity.

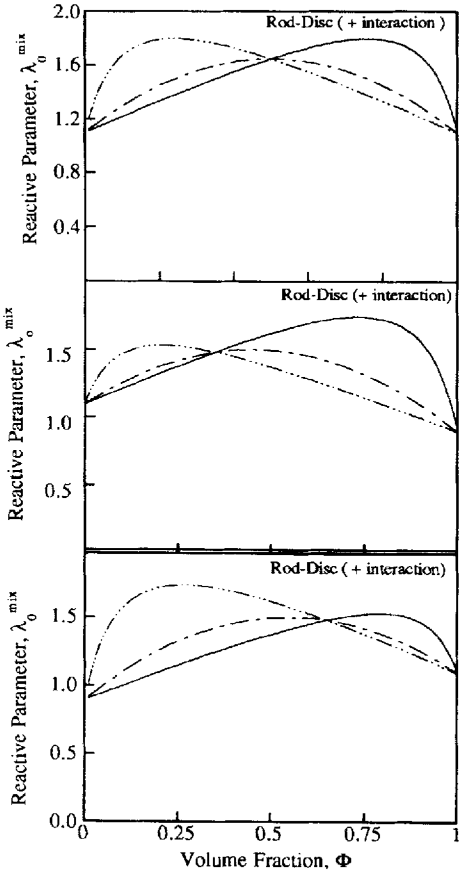

Figure 8. Biaxial rod–disc mixtures with positive dynamic couplings. Mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ; top figure: two aligning components ($\lambda^n = -\lambda^m = 1{\cdot}1$); middle figure: a mixture of non-aligning rods ($\lambda^n = 0{\cdot}9$) with aligning discs ($\lambda^m = -1{\cdot}1$); bottom figure: mixture of aligning rods ($\lambda^n = 1{\cdot}1$) with non-aligning discs ($\lambda^m = -0{\cdot}9$); R: 0·1 (full line), 1 (dashed-dot line), and 10 (dashed-triple dot line). Alignment transitions are predicted for mixtures of aligning–non-aligning (middle and bottom figure) components. The other case (top figure) show no crossover. The figure shows that positive interactions promote alignment.

The alignment transition observed in mixtures of aligning rods (discs) and non-aligning discs (rods) occurs at

$$R = \frac{\gamma_1^n}{\gamma_1^m} = \frac{(\Phi - 1) - \lambda^m(1 - \Phi^2)}{\Phi[1 - (2 - \Phi)\lambda^n]}. \qquad (35)$$

Figure 9 shows the viscosity ratio $R = \gamma_1^n/\gamma_1^m$ as a function of the volume fraction Φ for $\lambda^n = 0{\cdot}9$ and $\lambda^m = -1{\cdot}1$ (full line) and $\lambda^n = 1{\cdot}1$ and $\lambda^m = -0{\cdot}9$ (dashed-dot line). The lines in the figure indicates the alignment transition for a given (R, Φ). Addition of non-aligning rods to aligning discs (full line) eventually leads to non-alignment, and the rod concentration at the alignment transition decreases with increasing R. Addition of non-aligning discs to aligning rods (dashed line) eventually leads to non-alignment, and the disc concentration at the alignment transition increases with increasing R. Comparing figures 9 and 7 it follows that positive interactions promote alignment and mixtures require a higher concentration of the non-alignment component to reach the alignment transition.

4.1.3. *Mixtures with negative dynamic interaction*

In this case $\Lambda^{nm} < 0, \Lambda^{mn} > 0$. To simplify the analysis we assume $\Lambda^{nm} = -\lambda^n < 0$, $\Lambda^{mn} = -\lambda^m > 0$. The mixture's reactive parameter λ_o^{mix} simplifies to

$$\lambda_o^{mix} = \frac{\Phi^2 \lambda^n R}{\Phi(R-1)+1} - \frac{(1-\Phi)^2 \lambda^m}{\Phi(R-1)+1}. \qquad (36)$$

Figure 10 shows the mixture reactive parameter λ_o^{mix} as a function of the volume fraction Φ; top figure: two

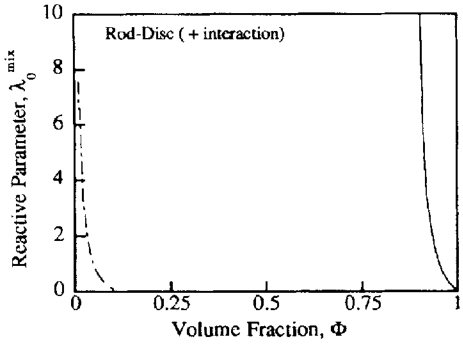

Figure 9. Biaxial rod–disc mixtures with positive dynamic couplings. Viscosity ratio $R = \gamma_1^n/\gamma_1^m$ as a function of the volume fraction Φ for $\lambda^n = 0{\cdot}9$ and λ^m: $-1{\cdot}1$ (full line) and $\lambda^n = 1{\cdot}1$ and λ^m: $-0{\cdot}9$ (dashed-dot line). The lines in the figure indicates the alignment transition for a given (R, Φ). Addition of non-aligning rods to aligning discs (full line) eventually leads to non-alignment, and the rod concentration at the alignment transition decreases with increasing R. Addition of non-aligning discs to aligning rods (dashed line) eventually leads to non-alignment, and the disc concentration at the alignment transition increases with increasing R. Positive interactions promote alignment.

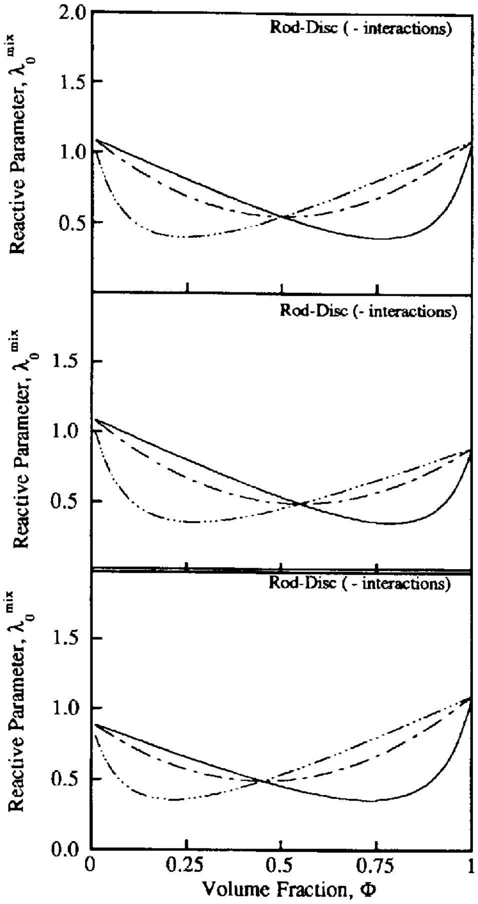

Figure 10. Biaxial rod–disc mixtures with negative dynamic couplings. Mixture reactive parameter $\lambda_{\mathrm{o}}^{\mathrm{mix}}$ as a function of the volume fraction Φ; top figure: two aligning components ($\lambda^{\mathrm{n}}=-\lambda^{\mathrm{m}}=1{\cdot}1$); middle figure: a mixture of non-aligning rods ($\lambda^{\mathrm{n}}=0{\cdot}9$) with aligning discs ($\lambda^{\mathrm{m}}=-1{\cdot}1$); bottom figure: mixture of aligning rods ($\lambda^{\mathrm{n}}=1{\cdot}1$) with non-aligning discs ($\lambda^{\mathrm{m}}=-0{\cdot}9$); R: 0·1 (full line), 1 (dashed-dot line), and 10 (dashed-triple dot line). Alignment transitions are predicted for all mixtures. Negative interactions promote non-alignment.

aligning components ($\lambda^{\mathrm{n}}=-\lambda^{\mathrm{m}}=1{\cdot}1$); middle figure: a mixture of non-aligning rods ($\lambda^{\mathrm{n}}=0{\cdot}9$) with aligning discs ($\lambda^{\mathrm{m}}=-1{\cdot}1$); bottom figure: mixture of aligning rods ($\lambda^{\mathrm{n}}=1{\cdot}1$) with non-aligning discs ($\lambda^{\mathrm{m}}=-0{\cdot}9$); R: 0·1 (full line), 1 (dashed-dot line), and 10 (dashed-triple dot line). The figure shows that alignment transitions (@ $\lambda_{\mathrm{o}}^{\mathrm{mix}}=+1$) are predicted for all mixtures. The figure shows that negative interactions promote non-alignment. The degree of asymmetry of the profiles increases when R deviates from unity.

The alignment transition observed in mixtures of aligning rods (discs) and non-aligning discs (rods) occurs at

$$R=\frac{\gamma_1^{\mathrm{n}}}{\gamma_1^{\mathrm{m}}}=\frac{(1-\Phi)[-(1-\Phi)\lambda^{\mathrm{m}}-1]}{\Phi(1-\Phi\lambda^{\mathrm{n}})}. \tag{37}$$

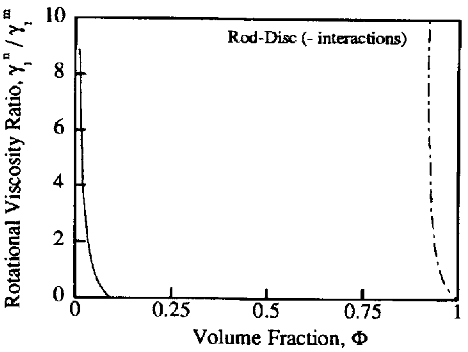

Figure 11. Biaxial rod–disc mixtures with negative dynamic couplings. Viscosity ratio $R=\gamma_1^{\mathrm{n}}/\gamma_1^{\mathrm{m}}$ as a function of the volume fraction Φ for $\lambda^{\mathrm{n}}=0{\cdot}9$ and λ^{m}: $-1{\cdot}1$ (full line) and $\lambda^{\mathrm{n}}=1{\cdot}1$ and λ^{m}: $-0{\cdot}9$ (dashed-dot line). The lines in the figure indicates the alignment transition for a given (R,Φ). Addition of small amounts of non-aligning rods to aligning discs (full line) leads to non-alignment, and the rod concentration at the alignment transition decreases with increasing R. Addition of small amounts of non-aligning discs to aligning rods (dashed line) leads to non-alignment, and the disc concentration at the alignment transition increases with increasing R. Negative interactions promote non-alignment.

Figure 11 shows the viscosity ratio $R=\gamma_1^{\mathrm{n}}/\gamma_1^{\mathrm{m}}$ as a function of the volume fraction Φ for $\lambda^{\mathrm{n}}=0{\cdot}9$ and $\lambda^{\mathrm{m}}=-1{\cdot}1$ (full line) and $\lambda^{\mathrm{n}}=1{\cdot}1$ and $\lambda^{\mathrm{m}}=-0{\cdot}9$ (dashed-dot line). The lines in the figure indicates the alignment transition for a given (R,Φ). Addition of small amounts of non-aligning rods to aligning discs (full line) leads to non-alignment, and the rod concentration at the alignment transition decreases with increasing R. Addition of small amounts of non-aligning discs to aligning rods (dashed line) leads to non-alignment, and the disc concentration at the alignment transition increases with increasing R. Comparing figures 9 and 11 it follows that negative interactions promote non-alignment and mixtures require a lower concentration of the non-alignment component to result in the mixture's non-alignment orientation mode.

5. Conclusions

A macroscopic continuum mechanical model for incompressible homogeneous binary nematic mixtures, under isothermal conditions has been presented. The model is an extension of Ericksen's transversely isotropic theory [18]. Special cases of the model are single component orthorhombic biaxial nematics and single component uniaxial nematics. The nematic mixture model accounts for the elasticity of the mixture that is assumed to be uniaxial or biaxial in the absence of flow. The theory is used to formulate mixture rules for the rotational viscosity and the reactive parameter. The mixture reactive parameter that governs the flow-alignment behaviour is a function of the concentration, the components rotational viscosity ratio, and the components reactive parameter. Uniaxial mixture rules are independent of dynamic interaction, but biaxial mixture rules are dependent on dynamic couplings. Uniaxial and biaxial mixtures of aligning and non-aligning nematics undergo alignment transitions at concentrations that depend on the components molecular weight ratio. Biaxial mixtures of two aligning nematics with negative dynamic interactions are non-aligning at an intermediate concentration range. The alignment properties of polymer–monomer nematic mixtures are dictated by the alignment properties of the polymer component.

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Appendix

A 1. *Tensorial coefficients*

The coefficients appearing in the expansions of $\mathbf{t}^s$, $\Phi\mathbf{N}$ and $(1-\Phi)\mathbf{M}$, appearing in equations ($8\,a$–c) are given by

$$\begin{aligned}L^{11}_{ijkl} = {} & \frac{\alpha^{11}_1}{2}(\delta_{il}\delta_{jk}+\delta_{ik}\delta_{jl}) \\ & + \frac{\Phi\alpha^{11}_2}{2}(n_in_k\delta_{jl}+n_jn_l\delta_{ik}+n_jn_k\delta_{il} \\ & + n_in_j\delta_{lk}+n_in_l\delta_{jk}) + \Phi\alpha^{11}_3 n_in_jn_kn_l \\ & + \frac{(1-\Phi)\alpha^{11}_4}{2}(m_im_k\delta_{jl}+m_jm_l\delta_{ik} \\ & + m_jm_k\delta_{il}+m_im_j\delta_{lk}+m_im_l\delta_{jk}) \\ & + (1-\Phi)\alpha^{11}_5 m_im_jm_km_l \\ & + (1-\Phi)\Phi\alpha^{11}_6(n_in_jm_km_l+m_im_jn_kn_l+n_im_jn_km_l \\ & + m_in_jm_kn_l+n_im_jm_kn_l\end{aligned} \tag{A 1}$$

$$\begin{aligned}L^{12}_{ijk} = {} & \Phi\frac{\alpha^{12}_1}{2}(n_i\delta_{jk}+n_k\delta_{ij}+n_j\delta_{ik}) \\ & + \Phi(1-\Phi)\alpha^{12}_2(n_im_jm_k+m_in_jm_k+m_im_jn_k),\end{aligned} \tag{A 2}$$

$$\begin{aligned}L^{13}_{ijk} = {} & (1-\Phi)\frac{\alpha^{13}_1}{2}(m_i\delta_{jk}+m_k\delta_{ij}+m_j\delta_{jk}) \\ & + \Phi(1-\Phi)\alpha^{13}_2(m_in_jn_k+n_im_jn_k+n_in_jm_k),\end{aligned} \tag{A 3}$$

$$L^{22}_{ij} = \Phi(1-\Phi)(\alpha^{22}_1\delta_{ij}+\alpha^{22}_2 n_in_j+\alpha^{22}_3 m_im_j), \tag{A 4}$$

$$L^{33}_{ij} = \Phi(1-\Phi)(\alpha^{33}_1\delta_{ij}+\alpha^{33}_2 n_in_j+\alpha^{33}_3 m_im_j) \tag{A 5}$$

and

$$\begin{aligned}L^{23}_{ij} = {} & \Phi(1-\Phi)\alpha^{23}_1[\Phi(1-\Phi)[n_im_j+n_jm_i]] \\ & + \Phi(1-\Phi)\alpha^{23}_3\delta_{ij}.\end{aligned} \tag{A 6}$$

A 2. *Constitutive equation for the extra stress tensor* (t)

In liquid crystals theories the extra stress tensor $\mathbf{t}$ is the sum of a symmetric contribution $\mathbf{t}^s$ and the antisymmetric contribution $\mathbf{t}^a$. To simplify the notation we define the two molecular fields $\mathbf{h}$ and $\mathbf{H}$ as

$$\begin{aligned}\mathbf{h} &\equiv -\frac{\partial F}{\partial \mathbf{n}} = -\kappa(\mathbf{n}\cdot\mathbf{m})[\mathbf{m}-(\mathbf{n}\cdot\mathbf{m})\mathbf{n}]; \\ \mathbf{H} &\equiv -\frac{\partial F}{\partial \mathbf{m}} = -\kappa(\mathbf{n}\cdot\mathbf{m})[\mathbf{n}-(\mathbf{n}\cdot\mathbf{m})\mathbf{n}].\end{aligned} \tag{A 7 a, b}$$

Using equations (A 1, A 2, A 3 and $8\,a$) we find the symmetric contribution to the extra stress tensor $\mathbf{t}^s$:

$$\begin{aligned}\mathbf{t}^s = {} & \alpha^{11}_1\mathbf{D} + \Phi\alpha^{11}_2(\mathbf{D}\cdot\mathbf{nn}+\mathbf{nn}\cdot\mathbf{D}) + \Phi\alpha^{11}_3\mathbf{nn}(\mathbf{nn}:\mathbf{D}) \\ & + (1-\Phi)\alpha^{11}_4(\mathbf{D}\cdot\mathbf{mm}+\mathbf{mm}\cdot\mathbf{D}) \\ & + (1-\Phi)\alpha^{11}_5\mathbf{mm}(\mathbf{mm}:\mathbf{D}) \\ & + \Phi(1-\Phi)\alpha^{11}_6(\mathbf{nn}(\mathbf{D}:\mathbf{mm})+\mathbf{mm}(\mathbf{D}:\mathbf{nn}) \\ & + 2\mathbf{nm}(\mathbf{D}:\mathbf{nm})+2\mathbf{mn}(\mathbf{D}:\mathbf{nm})) \\ & - \Phi\frac{\alpha^{12}_1}{2}(\mathbf{nh}+\mathbf{hn}) - \Phi(1-\Phi)\alpha^{12}_2 \\ & \times(\mathbf{mm}(\mathbf{n}\cdot\mathbf{h})+\mathbf{nm}(\mathbf{m}\cdot\mathbf{h})+\mathbf{mn}(\mathbf{m}\cdot\mathbf{h})) \\ & - (1-\Phi)\frac{\alpha^{13}_1}{2}(\mathbf{mH}+\mathbf{Hm}) - \Phi(1-\Phi)\alpha^{13}_2 \\ & \times(\mathbf{nn}(\mathbf{m}\cdot\mathbf{H})+\mathbf{mn}(\mathbf{n}\cdot\mathbf{H})+\mathbf{nm}(\mathbf{n}\cdot\mathbf{H}))\end{aligned} \tag{A 8}$$

where terms proportional to δ are omitted, since they can be absorbed into a pressure term. To find the antisymmetric $\mathbf{t}^a$ contribution to the total extra stress tensor $\mathbf{t}$, we write equation (3) in a slightly different form:

$$\Delta = \mathbf{t}^s:\mathbf{D} + \mathbf{t}^a:\mathbf{W} + \mathbf{h}\cdot\Phi\dot{\mathbf{n}} + \mathbf{H}\cdot(1-\Phi)\dot{\mathbf{m}} \tag{A 9}$$

From the equivalence between (3) and (A 9) we find

$$\mathbf{t}^a:\mathbf{W} = -\mathbf{h}\cdot\Phi\mathbf{W}\cdot\mathbf{n} - \mathbf{H}\cdot(1-\Phi)\mathbf{W}\cdot\mathbf{m}. \tag{A 10}$$

Rearranging the right hand side we get

$$\mathbf{t}^a:\mathbf{W} = (\Phi\mathbf{hn}+(1-\Phi)\mathbf{Hm}):\mathbf{W} \tag{A 11}$$

and splitting the tensor within the parenthesis into symmetric and antisymmetric contributions we get

$$\begin{aligned}\mathbf{t}^a:\mathbf{W} = {} & \{[\tfrac{1}{2}\Phi(\mathbf{hn}+\mathbf{nh})+\tfrac{1}{2}(1-\Phi)(\mathbf{Hm}+\mathbf{mH})]\}:\mathbf{W} \\ & + \{\tfrac{1}{2}\Phi(\mathbf{hn}-\mathbf{nh})+\tfrac{1}{2}(1-\Phi)(\mathbf{Hm}-\mathbf{mH})\}:\mathbf{W}.\end{aligned} \tag{A 12}$$

Noticing that the first bracket gives no contribution (since it is symmetric while $\mathbf{W}$ is antisymmetric) we finally get

$$\mathbf{t}^{\mathrm{a}} = \tfrac{1}{2}\Phi(\mathbf{hn} - \mathbf{nh}) + \tfrac{1}{2}(1 - \Phi)(\mathbf{Hm} - \mathbf{mH}). \qquad (\mathrm{A}\,13)$$

Using equations (A 7 *a*, *b* and A 13) we find that for $\Phi = 1/2$ this model gives $\mathbf{t}^{\mathrm{a}} = 0$. It should be noted that models with a symmetric stress tensor can also be easily formulated.

A 3. *Derivation of the director equations*

Using equations (A 2, A 4, A 6 and A 7) and $\mathbf{n} \cdot \mathbf{N} = 0$, the expansion (8 *b*) for the corotational derivative $\Phi\mathbf{N}$ yields to second order in $\mathbf{n} \cdot \mathbf{m}$:

$$\begin{aligned}\Phi\mathbf{N} = {} & \Phi\alpha_1^{12}[\mathbf{D} \cdot \mathbf{n} - (\mathbf{D} : \mathbf{nn})\mathbf{n}] \\ & + \Phi(1 - \Phi)[2\alpha_2^{12}(\mathbf{D} : \mathbf{nm}) \\ & - \kappa(\alpha_1^{22} + \alpha_3^{22} + \Phi(1 - \Phi)\alpha_1^{23})(\mathbf{n} \cdot \mathbf{m})] \\ & \times [\mathbf{m} - (\mathbf{n} \cdot \mathbf{m})\mathbf{n}]. \qquad (\mathrm{A}\,14)\end{aligned}$$

Using the following relabelling in equation (A 14):

$$\alpha_1^{12} \equiv \lambda^{\mathrm{n}}, \quad 2\alpha_2^{12} \equiv \Lambda^{\mathrm{nm}}, \quad \alpha_1^{22} + \alpha_3^{22} + \Phi(1 - \Phi)\alpha_1^{23} = 1/\gamma_1^{\mathrm{n}} \qquad (\mathrm{A}\,15\,a, b, c)$$

we get the governing equation (9 *a*) for the director $\mathbf{n}$. The coefficient γ_1^{n} is the rotational viscosity for $\mathbf{n}$ in the mixture and is a function of $\Phi(1 - \Phi)$.

Using equations (A 3, A 5, A 6 and A 7) and $\mathbf{m} \cdot \mathbf{M} = 0$, the expansion (8 *c*) for $(1 - \Phi)\mathbf{M}$ yields to second order in $\mathbf{n} \cdot \mathbf{m}$:

$$\begin{aligned}(1 - \Phi)\mathbf{M} = {} & (1 - \Phi)\alpha_1^{13}[\mathbf{D} \cdot \mathbf{m} - (\mathbf{D} : \mathbf{mm})\mathbf{m}] \\ & + \Phi(1 - \Phi)[2\alpha_2^{13}(\mathbf{D} : \mathbf{nm}) \\ & - \kappa(\alpha_1^{33} + \alpha_2^{33} + \Phi(1 - \Phi)\alpha_1^{23})(\mathbf{n} \cdot \mathbf{m})] \\ & \times (\mathbf{n} - (\mathbf{n} \cdot \mathbf{m})\mathbf{m}]. \qquad (\mathrm{A}\,16)\end{aligned}$$

Using the following relabelling in (A 16):

$$\alpha_1^{13} \equiv \lambda^{\mathrm{m}}, \quad 2\alpha_2^{13} \equiv \Lambda^{\mathrm{mn}}, \quad \alpha_1^{33} + \alpha_2^{33} + \Phi(1 - \Phi)\alpha_1^{23} \equiv 1/\gamma_1^{\mathrm{m}} \qquad (\mathrm{A}\,17\,a, b, c)$$

we get the governing equation (9 *b*) for the director $\mathbf{m}$. The coefficient γ_1^{m} is the rotational viscosity for $\mathbf{m}$ in the mixture and is a function of $\Phi(1 - \Phi)$.

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