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TOPICAL REVIEW

Non-equilibrium statistical mechanics of liquid crystals: relaxation, viscosity and elasticity

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Abstract

The rotational diffusion of a general-shape object (a molecule) in a flow of uniaxial nematic liquid crystal is considered in the molecular field approximation. The full corresponding Fokker–Planck equation is derived, and then reduced to the limit of diffusion of orientational coordinates in a field of uniaxial nematic potential and the flow gradient. The spectrum of orientational relaxation times follows from this analysis. As a second main theme of this work, we derive a complete form of microscopic stress tensor for this molecule from the first principles of momentum balance. Averaging this microscopic stress with the non-equilibrium probability distribution of orientational coordinates produces the anisotropic part of the continuum Leslie–Ericksen viscous stress tensor and the set of viscous coefficients, expressed in terms of molecular parameters, nematic order and temperature. The axially-symmetric limits of long-rod and thin-disc molecular shapes allow comparisons with existing theories and experiments on discotic viscosity. The review concludes with more complicated aspects of nonlinear constitutive equations, microscopic theory of rotational friction and the case of non-uniform flow and director gradients.

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Contents

1. Introduction

On the continuum level, the dissipation of energy in a liquid flow is determined by the viscous stress tensor, which in the linear regime is proportional to the flow gradients with a factor of viscous coefficient. Kinetic theory of viscosity has the aim of deriving this stress tensor, and the viscous coefficients, from the molecular parameters, interaction forces and temperature, thereby relating the kinetic linear response coefficient to the thermal fluctuations in the medium. Kinetic theory of viscosity of classical isotropic liquids is based on a complicated and delicate analysis of pair correlation functions out of equilibrium; it has a famous history of successful developments [1–3] although by far not everything is understood in that field.

In this review, we describe an approach to non-equilibrium statistical theory describing the hydrodynamics of nematic liquid crystals, the liquids with a spontaneously broken orientational symmetry due to the anisotropic pair interactions between constituent particles (molecules). In developing the *nematodynamics* we aim to justify prevalent phenomenological theories and determine the underlying principles governing the orientational dynamics of the molecules under simple shear flow. From a fundamental perspective, such studies reveal physical insights which may help us to answer some of the most important questions in rheological studies of nematic liquid crystals: to what extent does shear flow affect the molecular alignments? What is the microscopic basis for nematic liquid crystals displaying flow-induced transitions into an ordered or unstable state? Such questions represent typical phenomena abundant in physics for which a simple physical analysis often reveals deep underlying principles, yet a detailed and rigorous solution is necessary to confirm the analysis.

From a more practical perspective, the inherent nature of nematic liquid crystals to acquire a preferred orientation of anisotropic molecules, and preserve it in the presence of flow, provides a natural advantage to these materials to be used as precursors for the manufacturing of high performance fibres. The preferred orientation and degree of alignment of the molecules are found to have a predominant effect on the mechanical and thermal properties of the materials, and the optimization and control of preferred alignment is of paramount importance. Unfortunately, a fundamental understanding of the factors affecting the development of preferred alignment is still lacking, which may hinder their further development.

In comparison to thermotropic nematics, i.e. dense liquids of anisotropic molecules, dilute suspensions of non-spherical particles are reasonably well understood [4–6]. The intrinsic viscosities of suspensions of oblate and prolate spheroids have been calculated allowing low volume fraction viscosity measurements to be used to estimate particle aspect ratio. Studies have been completed which extend the observations to the interactions of several particles. Models that include the influence of Brownian motion have also been developed [7]. The majority of these theoretical studies have focused on rod-shaped nematic molecules, as opposed to disc-shaped objects or a more general case of anisotropic molecules with uniaxial symmetry. A few notable exceptions are the studies of discotic viscosity by Volovik [8], using the Poisson brackets approach, and by Hess [9, 10], using the geometric affine-transformation idea and then allowing the non-perfect orientational order. Carlsson [11] has shown how the experimentally observed anomaly in flow alignment of discotic systems must be related to the relative signs and magnitudes of viscous coefficients, establishing their bounds. For all anisotropic shapes of particles suspended in a fluid, as the concentration of particles increases, they no longer rotate freely. Their motion becomes limited through excluded volume interactions as well as long range inter-particle and hydrodynamic forces. For particles with a large length/thickness ratio the effective excluded volume is much larger than their actual volume. As a result, their relative motion will be geometrically constrained, and the physics becomes non-trivial since many-particle correlations have to be considered. This situation will be applicable to a thermotropic nematic liquid as well, where all molecules are equivalent and strongly interacting with each other, thus demanding a consistent statistical–mechanical model. We note as an aside that a parallel approach to the microscopic constraints and resulting viscosity anisotropy in smectic liquid crystals has been developed as well [12].

In general, the orientation of the director in a flowing nematic is determined by four external influences which tend to compete with, and in the steady-state balance one another. The first effect is the influence of flow alignment; in the case of simple planar shear this tends to rotate the director until it lies almost, though not quite, in the direction in which the fluid is moving. Secondly there is the influence exerted by applied fields such as the magnetic fields. Thirdly there is the influence exerted by the solid surfaces which contain the liquid which affects the dynamics of thin layers (the strong anchoring effect). Finally the director alignment may be influenced by the curvature elasticity of the nematic itself. In this work, we will not consider the effects of external magnetic fields and surface anchoring effects, since we are primarily interested in the bulk property of the system subject to shear flow without imposing external fields.

There are traditionally two approaches towards studying the rheological behaviour of liquid crystalline materials: the *top–down* macroscopic theory based on classical mechanics such as the Leslie–Ericksen model [13, 14] or the time-dependent Ginzburg–Landau theory, and the *bottom–top* molecular theory employing statistical approach that aims to derive fundamental constitutive equations governing the dynamics of the variables we are interested in. The macroscopic models assume the system being close to equilibrium and consider the dynamics of the *slow variables* such as the director or the order parameter tensor, while a complete microscopic theory allows us to consider even nematic systems driven far from equilibrium. Such is the case for a *tumbling* nematic that is often observed in high shear flow regime. Phenomenological models have existed for a long time to account for this phenomenon (see the key reviews [15–17] for reference), but as we shall see later, this effect can be understood from a microscopic perspective as well.

Some of the earliest attempts on microscopic approach include works by Diogo and Martins [18]. They consider the viscosity coefficients to be proportional to the characteristic relaxation time which is related to the probability of overcoming the nematic potential barrier during molecular reorientation. Although such consideration does give microscopic expressions for the Leslie coefficients, their model was not constructed as a self-consistent statistical theory, and contains too many free parameters. Therefore, a more elaborate statistical theory was required. Following the pioneering work of Hess [4], outlining the principles of rotational Fokker–Planck equation in non-equilibrium anisotropic fluids, Doi [19] made a major step in developing the statistical model that describes the hydrodynamics of rod-like nematic liquid crystals. Their work relied on averaging the microscopic stress tensor over the non-equilibrium distribution function; however, their expression for the stress tensor was not accurate and gave only the symmetric part of it. To introduce antisymmetric elements to the stress tensor they invoke an external magnetic field in an ad hoc manner, which makes it hard to reconcile with intrinsic antisymmetric viscous stress naturally in liquid crystals in the absence of external field [20, 21]. Following that work, Osipov and Terentjev suggested another approach [22] which assumes that the overall non-equilibrium distribution function should consist of an original equilibrium part and an additional non-equilibrium part due to the flow gradients, but their derivation of microscopic stress tensor has not been complete and their derived Leslie coefficients are not always consistent with flow alignment experiments.

All these approaches either suffer from some theoretical shortcomings or they are confined to specific nematic systems composed only of long rod-like molecules. Although the later analysis is highly relevant to the rheology of liquid crystalline polymers [23], a more elaborate microscopic theory on the nematodynamics of spheroidal molecules will serve a greater purpose to a wider class of nematic systems. In reviewing this problem we generally follow the approach of [22], improving on several shortcomings and expanding the range of applicability. We are also motivated by recent interests in the studies of *discotic* nematic liquid crystals. To our present knowledge, there have been little theoretical studies for the case of discotic nematic liquid crystalline phases in shear flow, though lately there has been a revival in experimental and theoretical interests in these materials due to their applications in high performance fibres (e.g. mesophase pitch-based carbon fibres, Kevlar) [24, 25]. Another example that highlights many important technological applications in these materials is kaolin clay suspensions (plate-shaped particles) which have seen limited rheological characterization [26]. The work outlined in this review should assist in characterizing some of the main microstructure features and textures developed in these materials under flow.

The outline of this review is as follows. In section 2, we discuss theoretical concepts of non-equilibrium statistical physics and hydrodynamics which allow us to derive the kinetic equation governing the evolution of the orientation distribution function of the molecules. We also attempt to solve the kinetic equation which gives us the dominant orientation relaxation time. In section 3, we demonstrate how the microscopic stress tensor can be derived using classical equation of motion for fluids. In section 4, we put together the results of kinetic modelling and the microscopic dynamics to derive the average macroscopic stress tensor. Its coefficients are a complete set of the Leslie's coefficients, expressed in terms of molecular and order parameters. We discuss their validity, followed by a brief discussion on the unusual nonlinear effects which exist in discotic nematics only. Section 5 outlines attempts to derive the rotational frictional constant from a microscopic description, focusing primarily on discotic nematics. Finally in section 6, we consider more realistic situations when spatial inhomogeneities and domain structures (such as those with point defects or disclinations) exist in nematic liquid crystals, and construct a new molecular theory to account for the Ericksen stress in the complete Leslie–Ericksen theory, and the corresponding Frank elastic constants. We do not have a separate concluding section as each individual chapter ends with its own discussion and conclusions; there we also highlight the limitation of the current state of theory and open questions in this field.

2. Kinetic theory

In this section, we discuss some of the concepts of rotational diffusion and Brownian motion. We demonstrate that the dynamical evolution of a general uniaxially-anisotropic molecule in rotational motion in a nematic potential can be described essentially by a multi-phase variable Fokker–Planck equation. The solutions of the kinetic equation in the weak flow limit suggest a rich spectrum of relaxation times. The dominant relaxation mode depends linearly on the rotational friction constant and exhibits an Arrhenius activation dependence on the inter-molecular coupling strength.

2.1. Rotational Brownian motion and hydrodynamics

A nematic fluid contains many anisotropic molecules, all of similar size in a dense phase. On a mean-field level, each molecule can be considered to be immersed in a thermodynamic bath which acts as a source of background fluctuations. We can therefore consider each molecule to undergo rotational Brownian motion since it experiences a constant flux of stochastic torques. Historically, ideas or rotational diffusion go back to Debye [27, 28] who, following the Langevin theory of paramagnetism [29] and incorporating the new at the time ideas of Brownian motion [30], have studied permanent electric dipoles in rotary thermal motion. Debye's theory was viewed as a significant achievement and provided a foundation for the study of rotary diffusion, leading to a basic kinetic equation widely used for the modelling of fluctuating systems. It was later superseded by the Onsager theory [31], which itself was superseded by the work of Kirkwood [32]. In all these cases, however, the rigid-body molecule was considered a sphere. The problem of an arbitrary-shaped rigid body executing rotational Brownian dynamics is however a technically complicated one. The reason for this is at least three-fold : (1) rotations about different axes do not commute, (2) the range of relevant variables, the angles specifying the body's orientation, is finite. This introduces the peculiar nature of the topological constraints to the system. (3) Relation between angular velocity and angular momentum is tensorial, not vectorial, as in translational motion.

Despite these complications, the rotational Brownian motion in a mean-field potential is thoroughly described within the framework of Smoluchowski equation. Jeffery [33], Hinch [7], Hess [4] and Maguire [34] solved similar problems for a dilute suspension of rod-like particles in a flow. We note that in addition to the rotational Brownian motion the molecules also execute translational random motions which we will not deal with in this review. The orientational degree of freedom is described by the dynamical variable $\boldsymbol{u}$, which is the unit vector defining the direction of principal axis (parallel to the long axis for rod-like molecules and perpendicular to the plane of a disc-like molecule).

The rotational Brownian motion can be best visualized as the trajectory of $\boldsymbol{u}(t)$ on the surface of the sphere defined by $|\boldsymbol{u}| = 1$. The movement of $\boldsymbol{u}(t)$ can be considered as random steps due to the thermal stochastic force and an external potential (see figure 1). The hydrodynamics of rotational motion can be addressed by first considering a general spheroid immersed in a stationary viscous liquid. We consider the molecule rotating with an angular velocity $\boldsymbol{\omega}$ by the influence of a torque $\boldsymbol{\Gamma}$ exerted by an external field $U(\boldsymbol{u})$. Consider a small

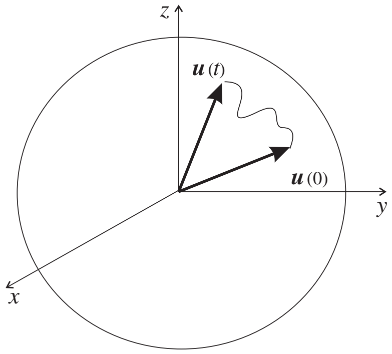

Figure 1. Rotational Brownian diffusion by the unit vector $\boldsymbol{u}$ along the molecular axis, which explores the space on the surface of unit sphere.

rotation $\delta\boldsymbol{\varphi}$ of the molecule that changes $\boldsymbol{u}$ to $\boldsymbol{u} + \delta\boldsymbol{\varphi} \times \boldsymbol{u}$. The work needed for this change is $-\boldsymbol{\Gamma} \cdot \delta\boldsymbol{\varphi}$, which must be equal to the change in U, i.e.,

$$-\boldsymbol{\Gamma} \cdot \delta\boldsymbol{\varphi} = U(\boldsymbol{u} + \delta\boldsymbol{\varphi} \times \boldsymbol{u}) - U(\boldsymbol{u}) = (\delta\boldsymbol{\varphi} \times \boldsymbol{u}) \cdot \frac{\partial U}{\partial \boldsymbol{u}} = \delta\boldsymbol{\varphi} \cdot \left(\boldsymbol{u} \times \frac{\partial U}{\partial \boldsymbol{u}}\right). \tag{1}$$

Hence

$$\Gamma_\beta = -\partial_\beta U, \qquad \text{where} \qquad \partial_\beta = \left(\boldsymbol{u} \times \frac{\partial}{\partial \boldsymbol{u}}\right)_\beta. \tag{2}$$

The operator ∂_β is called the rotational operator that plays the role analogous to the gradient operator ∇ in translational motion. Now if the molecules are immersed in a flowing medium, there will be a *residue* angular velocity (see Jeffrey [33] for details of separating the body uniform rotation). For a spheroid with aspect ratio $p = a/b$ this angular velocity is given by

$$\begin{aligned}
\boldsymbol{\Omega} &= \boldsymbol{u} \times \left\{ \frac{p^2}{p^2+1} \boldsymbol{g} \cdot \boldsymbol{u} - \frac{1}{p^2+1} \boldsymbol{g}^{\mathsf{T}} \cdot \boldsymbol{u} \right\} \\
&= \boldsymbol{u} \times \left\{ \frac{1}{2} \left(\frac{p^2}{p^2+1} \right) (\boldsymbol{g}^s + \boldsymbol{g}^a) \cdot \boldsymbol{u} - \frac{1}{2} \frac{1}{p^2+1} (\boldsymbol{g}^s + \boldsymbol{g}^a)^{\mathsf{T}} \cdot \boldsymbol{u} \right\} \\
&= \frac{1}{2} \frac{p^2-1}{p^2+1} (\boldsymbol{u} \times \boldsymbol{g}^s \cdot \boldsymbol{u}) + \frac{1}{2} (\boldsymbol{u} \times \boldsymbol{g}^a \cdot \boldsymbol{u}) \\
&= \frac{1}{2} \frac{p^2-1}{p^2+1} (\boldsymbol{u} \times \boldsymbol{g}^s \cdot \boldsymbol{u}) + \frac{1}{2} \nabla \times \boldsymbol{v} - \frac{1}{2} (\boldsymbol{u} \cdot \nabla \times \boldsymbol{v}) \boldsymbol{u}
\end{aligned} \tag{3}$$

where $g_{\alpha\beta}$ is the velocity gradient $\nabla_\beta v_\alpha$, and $g^s_{\alpha\beta}$ and $g^a_{\alpha\beta}$ are the symmetric and asymmetric part of this velocity gradient, respectively. Note that $\boldsymbol{\Omega}$ is perpendicular to $\boldsymbol{u}$.

2.2. Langevin equation

The stochastic effects on the particle's rotational motion a in viscous medium can be considered in a coherent fashion using the method of Langevin stochastic equation and the Fokker–Planck kinetic equation. The latter allows us to find explicit dynamical evolution of the distribution function in terms of the orientation of the director. To see how this can be applied to anisotropic fluid motion we first consider the dynamical equations of motion for the particle's angular velocity.

We first note that we can always diagonalize the moment of inertia tensor of a uniaxial particle; in the frame-independent form:

$$I_{\alpha\beta} = I_{\perp}\delta_{\alpha\beta} + (I_{\parallel} - I_{\perp})u_{\alpha}u_{\beta} \tag{4}$$

where $\boldsymbol{u}$ is the unit vector of molecule's principal axis. The instantaneous angular velocity of the molecule is

$$\dot{\boldsymbol{\Psi}} = \dot{\psi}\boldsymbol{u} + \boldsymbol{\omega} \tag{5}$$

where the first term on the right-hand side denotes angular velocity about the molecular axis, while $\boldsymbol{\omega}$ is the transverse angular velocity due to rotational motion perpendicular to the molecular axis, i.e. $\boldsymbol{\omega} \perp \boldsymbol{u}$.

For a molecule moving with an instantaneous angular momentum $\boldsymbol{L}$, we can immediately write down its expression,

$$L_{\alpha} = I_{\alpha\beta}\dot{\Psi}_{\beta} = I_{\parallel}\dot{\psi}u_{\alpha} + I_{\perp}\omega_{\alpha}. \tag{6}$$

The rotational motion thus obeys the equation of motion:

$$\dot{L}_{\alpha} = I_{\parallel}\ddot{\psi}u_{\alpha} + I_{\perp}\dot{\omega}_{\alpha} + I_{\parallel}\dot{\psi}\dot{u}_{\alpha}. \tag{7}$$

The first two terms on the right-hand side are the expected rotational torques about $I_{\parallel}$ and $I_{\perp}$ respectively, while the last term represents the *gyroscopic effect*. This term vanishes for the case of an infinitely long and thin rod ($I_{\parallel} \ll I_{\perp}$) but may be large for disc-like molecules. We will soon see that this term gives rise to non-trivial modifications to the kinetic equation and the stress tensor.

At this stage, we have to be careful about the meaning of $\boldsymbol{\omega}$. To evaluate all physical observables in the laboratory frame we have to make a coordinate transformation from the body's frame to the laboratory frame. Therefore for a molecule rotating with an instantaneous angular velocity $\dot{\boldsymbol{\Psi}}$, the transverse angular velocity $\boldsymbol{\omega}$ in the body frame is transformed in the following manner:

$$\left.\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}t}\right|_{\mathrm{lab}} = \dot{\boldsymbol{\Psi}} \times \boldsymbol{\omega} + \left.\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}t}\right|_{\mathrm{body}} = -\dot{\psi}\dot{\boldsymbol{u}} + \boldsymbol{u} \times \ddot{\boldsymbol{u}}. \tag{8}$$

Having obtained the general equation of motion in equation (7), we can write down the Langevin equation in terms of a vector stochastic torque $\boldsymbol{\xi}$ and a possible external torque $\boldsymbol{\Gamma}$,

$$\begin{aligned}\dot{L}_{\alpha} &= I_{\parallel}\ddot{\psi}u_{\alpha} + I_{\perp}\dot{\omega}_{\alpha} + I_{\parallel}\dot{\psi}\dot{u}_{\alpha} \\ &= -\lambda_{\alpha\beta}(\dot{\psi}u_{\beta} + \omega_{\beta} - \Omega_{\beta}) + \Gamma_{\alpha} + \xi_{\alpha}\end{aligned} \tag{9}$$

where $\lambda_{\alpha\beta} = \lambda_{\perp}\delta_{\alpha\beta} + (\lambda_{\parallel} - \lambda_{\perp})u_{\alpha}u_{\beta}$ is the uniaxial frictional constant tensor and the vector $(\dot{\psi}u_{\beta} + \omega_{\beta} - \Omega_{\beta})$ is the net angular velocity of the molecule relative to that of the reservoir, which is given by (3).

To get the equation of motion for the dynamical variable $\dot{\psi}$, we can multiply the above equation by u_{α} to eliminate the gyroscopic term,

$$I_{\parallel}\ddot{\psi} = -\lambda_{\parallel}\dot{\psi} + (\boldsymbol{\Gamma}\cdot\boldsymbol{u}) + (\boldsymbol{\xi}\cdot\boldsymbol{u}) \tag{10}$$

where we used the fact that both ω's are perpendicular to $\boldsymbol{u}$. Equation (10) is the equation of motion for the dynamical variable $\dot{\psi}$ dictating the angular rotation about the molecular axis.

Substituting (10) into equation (9) we obtain a similar equation of motion for the transverse angular velocity $\boldsymbol{\omega}$,

$$\begin{aligned}I_{\perp}\dot{\omega}_{\alpha} = {}& -(\delta_{\alpha\beta} - u_{\alpha}u_{\beta})\lambda_{\beta l}(\omega_{l} - \Omega_{l}) + (\delta_{\alpha\beta} - u_{\alpha}u_{\beta})\Gamma_{\beta} \\ & + (\delta_{\alpha\beta} - u_{\alpha}u_{\beta})\xi_{\beta} - I_{\parallel}\dot{\psi}(\boldsymbol{\omega}\times\boldsymbol{u})_{\alpha}.\end{aligned} \tag{11}$$

Note the natural occurrence of the perpendicular projection operators $\delta_{\alpha\beta} - u_{\alpha}u_{\beta}$ in this expression.

2.3. *Generalized Fokker–Planck equation*

The rotational diffusion of the anisotropic molecules is captured by the Fokker–Planck equation which describes the dynamical evolution in time of the system's phase-space distribution function $W(\boldsymbol{\omega}, \dot{\psi}, \boldsymbol{u}, t)$ [35]:

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial u_\alpha}(\dot{u}_\alpha W) - \frac{\partial}{\partial \omega_\alpha}(\dot{\omega}_\alpha W) - \frac{\partial}{\partial \dot{\psi}}(\ddot{\psi} W) + \frac{1}{2}\frac{\partial^2}{\partial \omega_\alpha \partial \omega_\beta} \times \left[\frac{1}{I_\perp^2}\langle(\xi_\alpha - u_\alpha \xi_\gamma u_\gamma)(\xi_\beta - u_\beta \xi_\mu u_\mu)\rangle W\right] + \frac{1}{2}\frac{\partial^2}{\partial \dot{\psi}^2}\left[\frac{1}{I_\parallel^2} u_\alpha \Xi^\psi_{\alpha\beta} u_\beta W\right] \qquad (12)$$

where $\Xi^\psi_{\alpha\beta}(t - t') = \langle \xi_\alpha(t) \xi_\beta(t')\rangle$ is the correlation function between the vector stochastic torque ξ that perturbs $\dot{\psi}$. It can be shown directly that the following form for $\Xi^\psi_{\alpha\beta}$ indeed satisfies the fluctuation–dissipation theorem,

$$\Xi^\psi_{\alpha\beta} = \Xi_\perp \delta_{\alpha\beta} + (\Xi_\parallel - \Xi_\perp) u_\alpha u_\beta. \qquad (13)$$

2.3.1. Reduced Fokker–Planck equation. We next consider obtaining the coordinate dependence of the distribution function. We note that there are intrinsically two time-scales of interest, usually separated by a significant margin in liquids (section 5 has a much more extended discussion of these characteristic times, also applicable to the translational motion). The first of these scales is a fast relaxation time after which the system reaches the equilibrium Maxwell velocity distribution, given by the balance of inertial and friction parameters:

$$\tau_\omega = \frac{I_\perp}{\lambda_\perp}. \qquad (14)$$

The second is the relatively slow relaxation time

$$\tau_u = \frac{(\triangle\theta)^2}{2D_r} \qquad (15)$$

after which the system reaches the equilibrium Boltzmann distribution of its angular coordinates, essentially controlled by the corresponding diffusion rate. $\triangle\theta$ is the free angular volume the molecule rotates in the diffusion limit and D_r is the rotational diffusion constant related to the microscopic friction constants via the fluctuation–dissipation theorem. This is the characteristic time for the relaxation of fluctuations of the system back to equilibrium under Brownian forces. Their ratio we define as a small parameter:

$$\alpha^2 = \frac{\tau_\omega}{\tau_u} = \frac{2kTI_\perp}{\lambda_\perp^2} \ll 1 \qquad (16)$$

where we omit the dimensionless term $(\triangle\theta)^2$. The smallness of α is not obvious at this stage, but will become apparent later. Substituting the dynamic part of equations (10) and (11) into equation (12), and introducing the dimensionless variables:

$$\tau = \frac{\lambda_\perp}{I_\perp} t, \qquad \omega' = \sqrt{\frac{I_\perp}{kT}}\,\omega, \qquad \dot{\psi}' = \sqrt{\frac{I_\parallel}{kT}}\,\dot{\psi}, \qquad (17)$$

we obtain the dimensionless form for the generalized Fokker–Planck equation,

$$\frac{\partial W}{\partial \tau} + \alpha \partial_\beta(\omega'_\beta W) + \alpha \frac{\partial}{\partial \omega'_\beta}(\delta_{\alpha\beta} - u_\alpha u_\beta)\left(\frac{\Gamma_\beta}{kT} W\right) = \frac{\partial}{\partial \omega'_\alpha}\left[\omega'_\alpha - \Omega'_\alpha + \frac{1}{2}\frac{\partial}{\partial \omega'_\beta}(\delta_{\alpha\beta} - u_\alpha u_\beta) + \alpha A \dot{\psi}'(\boldsymbol{\omega}' \times \boldsymbol{u})_\alpha\right] W + \Delta A^2 \frac{\partial}{\partial \dot{\psi}'}\left(\dot{\psi}' - \phi + \frac{1}{2}\frac{\partial}{\partial \dot{\psi}'}\right) W \qquad (18)$$

with the shorthand notations

$$A = \sqrt{\frac{I_\parallel}{I_\perp}}, \qquad \Delta = \frac{\lambda_\parallel}{\lambda_\perp}, \qquad \phi = \frac{1}{2}\boldsymbol{u}\cdot\nabla\times\boldsymbol{v}. \tag{19}$$

To ease the notations we shall suppress the primes of ω' and ψ'; it will be explicitly indicated when we return to full-dimensional variables later on.

2.3.2. Elimination of fast variables. We now describe in a qualitative fashion the meanings of the two time-scales introduced in the previous section. The situation where the variables describing a phenomenon can be divided into two sets, one evolving on a rapid time-scale and one evolving on a slow time-scale, is of frequent occurrence in physics. It is often desirable to eliminate or average over the rapid variables in order to study the dynamics of the slow variables. Such coarse-graining is done by assuming that the velocity distribution of the Brownian particle rapidly thermalizes while the coordinate distribution remains far from equilibrium for a much longer time. This means that the velocity distribution is close to a Maxwell distribution while the position distribution still has not evolved too far from the initial distribution. The equation, obtained after integrating out the fast variables by estimating the phase distribution function to be the product of the reduced distribution function in terms of the slow variable and a Maxwell distribution for fast variables, is formally known as the Smoluchowski equation [36]. We note that some authors use the term 'Fokker–Planck equation' interchangeably with 'Smoluchowski equation'. Here we distinguish (after the original papers of Fokker [37] and Planck [38]) the case when the additional degrees of freedom represent velocity, strictly reserving the term 'Smoluchowski equation' for cases in which the degrees of freedom represent position or configuration (after Smoluchowski [39]). The basic assumption that allows this distinction is that thermalization of velocities occurs on a time-scale short with respect to the time for appreciable changes in the positional distribution; it is almost always satisfied in the high friction (overdamped) limit.

We can apply the above concepts to the case of a nematic to obtain the coordinate-only Smoluchowski equation. The fast variables in this case are the angular velocity both along and perpendicular to the director axis ($\boldsymbol{\omega}$ and $\dot{\psi}$) while the slow variable is the angular orientation $\boldsymbol{u}(t)$. Assuming the quasi-equilibrium state when the longitudinal angular velocity distribution function has thermalized, we can approximate

$$W(\boldsymbol{\omega}, \dot{\psi}, \boldsymbol{u}, t) = \exp\left\{-\tfrac{1}{2}(\dot{\psi} - \phi)^2\right\} W'(\boldsymbol{\omega}, \boldsymbol{u}, t). \tag{20}$$

Substituting this into equation (18) and integrating over $\dot{\psi}$ eventually gives the angular velocity dependence of $W'(\boldsymbol{\omega}, \boldsymbol{u}, t)$:

$$\begin{aligned}\dot{W}' &= \alpha\partial_\beta(\omega_\beta W') + \alpha\frac{\partial}{\partial\omega_\beta}(\delta_{\alpha\beta} - u_\alpha u_\beta)\frac{\Gamma_\beta}{kT}W' \\ &= \alpha A\phi(\boldsymbol{u})\frac{\partial}{\partial\omega_\beta}[(\boldsymbol{\omega}\times\boldsymbol{u})_\beta W'] + \frac{\partial}{\partial\omega_\alpha}\left[\omega_\alpha - \Omega_\alpha + (\delta_{\alpha\beta} - u_\alpha u_\beta)\frac{\partial}{\partial\omega_\beta}\right]W'.\end{aligned}$$

Introducing a relative velocity $\mathcal{O}_\alpha = \omega_\alpha - \Omega_\alpha$, we may naively proceed with integration over the remaining fast variable $\boldsymbol{\omega}$ using

$$W'(\boldsymbol{\omega}, \boldsymbol{u}, t) = \mathrm{e}^{-\frac{1}{2}\mathcal{O}^2} w(\boldsymbol{u}, t). \tag{21}$$

This however gives the trivial equation

$$\dot{w} + \alpha\partial_\beta(\Omega_\beta w) = 0 \tag{22}$$

with the diffusion term missing from the equation. We conclude that the non-trivial Smoluchowski equation with the required diffusion term must come from adding small corrections to the distribution function that contains the 'last bits' of non-relaxed Maxwell distribution. Hence we suggest that

$$W'(\boldsymbol{\omega}, \boldsymbol{u}, t) = \mathrm{e}^{-\frac{1}{2}\mathcal{O}^2}\left[w(\boldsymbol{u}, t) + \alpha y(\boldsymbol{O}, \boldsymbol{u})\right] \tag{23}$$

where the smallness is controlled by the natural parameter—the ratio of relaxation times $\alpha \ll 1$, and the form of the correction term $y(\boldsymbol{O}, \boldsymbol{u})$ is to be determined self-consistently. Using (23) instead of (21), and neglecting terms of second orders in α, the equation transforms into

$$\dot{w}(\boldsymbol{u}, t) + \alpha\Omega_\beta\partial_\beta w + \alpha\mathcal{O}_\beta\left[\partial_\beta w + \Omega_\alpha\partial_\alpha\Omega_\beta w - \frac{\Gamma_\beta}{kT}w + A\phi(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w\right]$$
$$+\alpha\mathcal{O}_\alpha\mathcal{O}_\beta\partial_\alpha\Omega_\beta w = \alpha(\delta_{\alpha\beta} - u_\alpha u_\beta)\left[\frac{\partial^2 y}{\partial\mathcal{O}_\alpha\partial\mathcal{O}_\beta} - \mathcal{O}_\alpha\frac{\partial y}{\partial\mathcal{O}_\beta}\right].$$

Assuming that $y = a + b_i\mathcal{O}_i + c_{ij}\mathcal{O}_i\mathcal{O}_j$ we determine uniquely the coefficients b_i and c_{ij}

$$c_{ij} = -\frac{1}{2}w\partial_i\Omega_j \tag{24}$$

$$b_j = -\partial_j w - \omega_i(\partial_i\Omega_j)w + \frac{\Gamma_j}{kT}w - A\phi(\boldsymbol{u})(\boldsymbol{\Omega}\times\boldsymbol{u})_j w. \tag{25}$$

Integrating over the fast variable of relative angular velocity $\mathcal{O}_i$, we finally have the desired dimensionless Smoluchowski's equation for the coordinate-only distribution function $w(\boldsymbol{u}, t)$, which we will call here the *orientational distribution function*:

$$\dot{w} + \alpha\partial_\beta(\Omega_\beta w) = \alpha^2\partial_\beta\left(\partial_\beta w - \frac{\Gamma_\beta}{kT}w\right) + \alpha^2\partial_\beta(\Omega_\alpha\partial_\alpha\Omega_\beta w)$$
$$+\frac{A}{2}\alpha^2\partial_\beta[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w] + \alpha^2\partial_\beta[\Omega_\alpha(\partial_\alpha\Omega_\beta)w]. \tag{26}$$

The right-hand side now contains small but non-vanishing terms proportional to α^2 (compare with equation (22) where this was missing in the leading order in α). The first term on the right-hand side gives the diffusional term in a non-equilibrium system with external potential, which describes rotational diffusion mechanism. The term $\alpha\partial_\beta(\Omega_\beta w)$ incorporates the linear effects of perturbation due to external flow.

2.3.3. Nonlinear effects. The last two terms in equation (26) deserve further discussion. We note that these terms have not been shown in previous work, e.g. [19, 22], but their presence is necessary to describe novel nonlinear effects due to higher flow and intrinsic geometrical shape of the molecules. The term $\frac{1}{2}\alpha^2 A\partial_\beta[(\boldsymbol{u}\cdot\boldsymbol{\nabla}\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w]$ reveals the gyroscopic motion of the molecules due to the non-vanishing moment of inertia along the molecular axis. This term is commonly neglected for thin rods with $A = \sqrt{I_\parallel/I_\perp} \ll 1$. This however is not the case for a discotic, when $I_\parallel$ and $I_\perp$ are comparable. One expects that this gyroscopic effect will contribute essentially to the viscous torques and the antisymmetric stress tensor, and modify the 'shape' of the equilibrium distribution function. This conjecture will be pursued and verified in a quantitative fashion in section 4.

On the other hand, the second term $\alpha^2\partial_\beta[\Omega_\alpha(\partial_\alpha\Omega_\beta)w]$ arises as a result of algebra. This term vanishes in the weak-flow limit (small $\boldsymbol{\Omega}$) and will be present in both isotropic and anisotropic liquids. It therefore constitutes more trivial higher order corrections to the overall stress tensor due to stronger external flow. It may explain the changes in the linear viscosity for a general spheroidal nematic before tumbling sets in, where the whole physical basis of the linear model breaks down, but it does not introduce any new symmetries into the problem.

2.4. Solving the kinetic equation

There is an intrinsic time-scale that may be related to the typical relaxation times of the orientational distribution function which may be obtained via solving the kinetic equation. In fact, as we will see shortly, the solutions give rise to a spectrum of relaxation times that relate to the relaxation of the various normal modes of angular rotations. This relaxation can be observed macroscopically in the relaxation spectrum of the order parameter [40].

The standard way to solve the nonlinear integral kinetic equation in the angular space is to expand the distribution function in spherical harmonics and solve the resulting equations for the expansion coefficients sometimes numerically. Although this method is always available, we can gain some insights by solving it analytically using a simple eigenfunction expansion. For the sake of simplicity, we rewrite the Smoluchowski equation (26) in *zero flow*, in the following form:

$$\frac{\partial w}{\partial t} = -\Lambda(\boldsymbol{u}) w(\boldsymbol{u}, t) \tag{27}$$

where $\Lambda(\boldsymbol{u})$ is a linear differential operator:

$$\Lambda(\boldsymbol{u}) w(\boldsymbol{u}, t) = -\alpha^2 \partial_k \left(\partial_k w + \frac{\partial_k U}{kT} \, w \right). \tag{28}$$

Let w_n be the eigenfunctions

$$\Lambda(\boldsymbol{u}) w_n = \mu_n w_n. \tag{29}$$

Expanding the distribution function in terms of the complete orthogonal set of eigenfunctions:

$$w(\boldsymbol{u}, t) = \sum_n a_n(t) \, w_n(\boldsymbol{u}), \tag{30}$$

we obtain the time dependence of coefficients $a_n(t)$, $a_n(t) = a_n(0)\, \mathrm{e}^{-\mu_n t}$. The equilibrium distribution function $w_{eq}(\boldsymbol{u})$ is an eigenfunction which by definition has infinite relaxation time. The eigenvalue being the inverse of the relaxation time therefore is 0, corresponding to the eigenfunction w_0 with $n = 0$. Therefore, the full solution takes the form

$$w(\boldsymbol{u}, t) = w_{eq}(\boldsymbol{u}) + \sum_{n=1} a_n(0)\, \mathrm{e}^{-\mu_n t} \, w_n(\boldsymbol{u}) \tag{31}$$

where $a_0 = 1$ by normalization. Since in statistical equilibrium $\dot{w}_{eq} = 0$, substituting equation (31) into (27) gives

$$\partial_k \left[\partial_k w_n + \frac{\partial_k U(\boldsymbol{u} \cdot \boldsymbol{n})}{kT} w_n \right] = -\frac{\mu_n}{\alpha^2} w_n \tag{32}$$

where $U(\boldsymbol{u} \cdot \boldsymbol{n})$ is the mean-field potential, which depends on the polar angle θ only. Equation (32) is very similar to solving the Schrödinger's equation in quantum mechanics. In this case, the external potential has to be modified. This mapping is formally known as the Darboux transformation or supersymmetry [41]. The operator of course has to be made Hermitian but this can be achieved through a simple transformation [42].

Expanding the rotational operator ∂_k in spherical coordinates and writing the eigenfunction of (32) as $w_n = f_n(\theta) w_{eq}$, where $w_{eq} \equiv \exp(-U(\theta)/kT)$, we finally obtain the following differential equation :

$$\frac{\partial^2 f_n}{\partial \theta^2} + \left(\cot\theta - \frac{1}{kT} \frac{\partial U}{\partial \theta} \right) \frac{\partial f_n}{\partial \theta} = -\frac{\mu_n}{\alpha^2} f_n. \tag{33}$$

f_n depends on θ since, for rotations of a spheroid, the general solution of equation (33) must be an eigenfunction expansion in terms of the Legendre polynomials $P_n(\cos\theta)$. Equation (33) can be rearranged to give

$$\frac{\mathrm{e}^{U(\theta)/kT}}{\sin\theta}\frac{\partial}{\partial\theta}\left[\mathrm{e}^{U(\theta)/kT}\sin\theta\frac{\partial f_n}{\partial\theta}\right] = -\frac{\mu_n}{\alpha^2}f_n. \tag{34}$$

Rearranging the equation further and taking care of the constants of integration, we finally obtain the following self-consistent integral equation:

$$f_n(\theta) = C - \frac{\mu_n}{\alpha^2}\int_0^\theta \frac{\mathrm{e}^{U(x)/kT}}{\sin x}\,\mathrm{d}x\int_0^x w_n(z)\sin z\,\mathrm{d}z. \tag{35}$$

Multiplying $\mathrm{e}^{-U(\theta)/kT}$ on both sides of the equation,

$$w_n(\theta) = \mathrm{e}^{-U(\theta)/kT}\left[C - \frac{\mu_n}{\alpha^2}\int_0^\theta \frac{\mathrm{e}^{U(x)/kT}}{\sin x}\,\mathrm{d}x\int_0^x w_n(z)\sin z\,\mathrm{d}z\right]. \tag{36}$$

At this stage, we introduce the method of iterations [41]:

$$w_n(\theta) = w_0 + \frac{\mu_1}{\alpha^2}w_1 + \left(\frac{\mu_1}{\alpha^2}\right)^2 w_2 + \cdots \tag{37}$$

where μ_1 is the smallest non-vanishing coefficient corresponding to the first eigenfunction w_1. This method will be justified later, when the perturbation coefficient μ_1/α^2 is shown to be small.

Substituting the solution with only the leading terms in μ_1 and comparing the terms explicitly, we have the relation

$$w_n(\theta) = \mathrm{e}^{-U(\theta)/kT}\,\mathrm{e}^{-U(0)/kT}w_0(0)\left[1 - \frac{\mu_1}{\alpha^2}\int_0^\theta \frac{\mathrm{e}^{U(x)/kT}}{\sin x}\,\mathrm{d}x\int_0^x \mathrm{e}^{-U(z)/kT}\sin z\,\mathrm{d}z\right]. \tag{38}$$

A conceivable boundary condition for any eigenfunction is that the distribution function must vanish at $\theta = \pi$, i.e., $w_n(\pi) = 0$, as it must do since $w_n(\theta)$ is a single-valued function. This boundary condition gives

$$1 - \frac{\mu_1}{\alpha^2}\int_0^\pi \frac{\mathrm{e}^{U(x)/kT}}{\sin x}\,\mathrm{d}x\int_0^x \mathrm{e}^{-U(z)/kT}\sin z\,\mathrm{d}z = 0. \tag{39}$$

The integrals can be evaluated using the saddle-point approximation. In Maier–Saupe mean-field approximation, $U(\theta) = -JS_2\cos^2(\theta)$, where J denotes the mean-field coupling strength (an explicit form for the energy constant J will be discussed in section 5) and S_2 is the principle scalar order parameter of uniaxial nematic phase, discussed in much greater detail in section 4. The ratio $q = JS_2/kT \simeq 4.5$ at the nematic transition, hence justifying the method of saddle-point approximation where $JS_2/kT \gg 1$. Recovering the full-dimensional form finally gives the following value for μ_1:

$$\mu_1 = \frac{4}{\pi}q^{\frac{3}{2}}\,\mathrm{e}^{-q}D_r = \frac{4}{\pi\lambda_\perp}\frac{(JS_2)^{3/2}}{(kT)^{1/2}}\,\mathrm{e}^{-JS_2/kT} \tag{40}$$

where $D_r = kT/\lambda_\perp$ is the rotational diffusion constant and $\lambda_\perp$ is the friction constant for the molecular rotation about any axis parallel to the plane of the disc. We now return to justifying the perturbation in terms of the small parameter μ_1/α^2. In dimensional form, we have

$$\frac{\mu_1}{\alpha^2} \longrightarrow \frac{\mu_1\lambda_\perp}{kT} = \frac{4}{\pi}q^{\frac{3}{2}}\,\mathrm{e}^{-q}. \tag{41}$$

This is indeed small in the limit of large q and justifies the perturbation expansion. The inverse of μ_1 gives the dominant (longest) relaxation time

$$\tau_1 = \frac{\pi}{4q^{3/2}D_r}\,\mathrm{e}^{q} = \frac{\pi\lambda_\perp}{4}\frac{(kT)^{1/2}}{(JS_2)^{3/2}}\,\mathrm{e}^{JS_2/kT} \tag{42}$$

which gives a dependence similar to the relaxation time for the molecular director correlation function $\langle \boldsymbol{u}(t)\boldsymbol{u}(0)\rangle = \mathrm{e}^{-t/\tau_r}$, where $\tau_r = \frac{1}{2}D_r$ is the rotational correlation time [23]. For a typical nematic liquid, $D_r \simeq 10^8\ \mathrm{s}^{-1}$, and $\tau_1 \simeq 10^{-7}$ s. This result agrees well with typical molecular relaxation times for the principal tumbling motion [43]. Also, this time-scale is usually small compared to the typical flow rate hence justifying the validity of the continuum Leslie–Ericksen description for nematics in flow (see section 3). In a passing remark, we note that this problem can also be solved in a simpler way, with inspiration from Kramers problem on a particle's passage over a potential barrier [41]. In other words, the relaxation mechanisms for rotational motion in liquid crystals are similar to the overcoming of the potential barriers imposed by the average medium in a mean-field.

The fact that the rotational diffusion of a nematic liquid crystal is associated with a rich spectrum of relaxation times is due to higher order modes of rotational motion contained in (37), involving spherical harmonics in azimuthal and polar coordinates. It could also be attributed to the generic non-spherical shape of the molecule and the anisotropic rotatory diffusion tensor. The various relaxation modes and times correspond to the non-collective relaxations around different symmetry axes of the molecules. This result agrees with Diogo's conclusion [18] that the relaxation times for the flipping motions of the molecules obey the Arrhenius law. The exponential factor accounts for the probability that the reorienting molecule has enough energy to overcome the potential barrier due to intermolecular nematic potential. In reality, however, we may need to consider the free volume effects which exist even in the absence of nematic potential. This would give rise to the *Vogel–Fulcher* type of glassy relaxation [44]. On the other hand, the explicit dependence of the relaxation time on the rotational friction constant is expected due to slow decay in the presence of high friction. A typical application of the rotational diffusion problem is observed in the dielectric relaxation of nematics in the presence of an external electric field [40, 43], where more than one Debye relaxation times are found corresponding to rotations around the long or short molecular axis. Similar phenomena are also observed via NMR [43].

3. Viscous stress tensor

In this section, we discuss the non-equilibrium transport phenomena in a nematic liquid. We briefly review the classical Leslie–Ericksen theory and then concentrate on the so-called microscopic stress tensor. This is a key concept describing the transfer of linear momentum of an individual anisotropic particle (molecule). We approach this discussion using classical kinetic theory of simple fluids, and then relate it to the macroscopic (observable) stress tensor.

3.1. Hydrodynamics of a uniaxial fluid

A nematic liquid crystal flows easily like a conventional liquid consisting of similar small molecules. The state of alignment however turns out to be rather complicated. In the first place, the flow depends on the angles the director makes with the flow direction and with the velocity gradient. Secondly, the translational motions are coupled to inner, orientational motions of the molecules. Consequently, in most cases the flow disturbs the alignments and causes the director to rotate. From the theoretical point of view the coupling between orientation and flow is a delicate matter.

The hydrodynamics for an isotropic classical fluid is well studied [2, 3]. The approach is to treat the fluid as a continuous medium and any small volume element is always assumed to be so large that it still contains a very great number of molecules. The dynamical situation is specified by the fluid velocity field $\boldsymbol{v}(\boldsymbol{r}, t)$, and by any two thermodynamic quantities

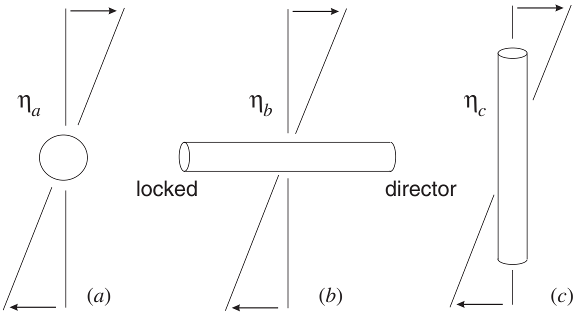

Figure 2. Three principal geometries of simple shear with a constant (fixed) director field, corresponding to the three Miesowicz coefficients.

pertaining to the fluid, for instance the pressure $p(\boldsymbol{r}, t)$ and the density $\rho(\boldsymbol{r}, t)$. The condition of incompressibility is always assumed, $\nabla \cdot \boldsymbol{v} = 0$. The equation of motion is then given by the linear Navier–Stokes form:

$$\rho \left[\frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v} \cdot \nabla)\boldsymbol{v} \right] = -\nabla p + \nabla \boldsymbol{\sigma}_{\text{visc}} \tag{43}$$

where the right-hand side denotes the total force, which comes from two contributions: the net pressure gradient and the viscous stress term. We have neglected the presence of additional external forces such as the potential term. The classical viscous stress is given by

$$\sigma_{\alpha\beta} = \eta \left(\frac{\partial v_\beta}{\partial x_\alpha} + \frac{\partial v_\alpha}{\partial x_\beta} \right) \equiv 2\eta g^s_{\alpha\beta} \tag{44}$$

where η is the viscosity coefficient.

For a simple shear flow in a nematic liquid, the measured viscosity coefficient depends on the orientation of the director $\boldsymbol{n}$. The direction of $\boldsymbol{n}$ can be specified by the angles ϕ and θ. If the orientation of the director is fixed by external forces (for instance by a strong magnetic field), we can define three geometries of simple shear as $\eta_a : \phi = 90^\circ\, \theta = 90^\circ$ for the director normal to the shear plane; $\eta_b : \phi = 0^\circ\, \theta = 0^\circ$ for director parallel to flow direction; $\eta_c : \phi = 0^\circ\, \theta = 90^\circ$ for the director parallel to velocity gradient (see figure 2). The three coefficients η_a, η_b and η_c are often called the Miesowicz coefficients.

3.2. Leslie–Ericksen theory

So far we have been concerned with the motion of a nematic liquid in which the orientation of the director is fixed. If we lift this restriction, we will have to consider an extra degree of freedom associated with the orientation of the director $\boldsymbol{n}(\boldsymbol{r}, t)$, which may introduce local unbalanced torques in the system. The phenomenological linear hydrodynamics of nematics is adequately described in the context of Leslie–Ericksen (LE) theory, by considering the entropy sources, due to all friction processes in the fluid. In short, and keeping the notation close to the definitive de Gennes' monograph [43], the LE approach describes the dissipation due to a decrease in the stored energy,

$$T\dot{S} = \int \left\{ \sigma^s_{\alpha\beta} g^s_{\alpha\beta} + h_\alpha N_\alpha \right\} \mathrm{d}^3\boldsymbol{r} \tag{45}$$

where $g^s_{\alpha\beta}$ denotes the symmetric velocity gradient and h_α is the molecular field, representing the local torque due to the variation of nematic director [43]. Also, the corotational derivative

$$\boldsymbol{N} = \dot{\boldsymbol{n}} - \boldsymbol{\nu} \times \boldsymbol{n} \tag{46}$$

represents the rate of change of the director with respect to the flow background, and $\boldsymbol{\nu} = \frac{1}{2}\nabla \times \boldsymbol{v}$ is the flow rotation angular velocity.

Another approach, proposed by the Harvard group [45], assumes that the velocity field is sufficient to specify the state, and the orientation of the director is deduced from the gradients of $\boldsymbol{v}$. In this picture, a rotation of the director can only occur in the presence of a non-uniform flow. There is however experimental evidence to show that this choice of state variable is not sufficient to describe a nematic, while the LE choice is adequate [46].

In irreversible processes, it is customary to write the entropy source as the product of 'flux' by the conjugate 'force' [47]. Choosing $\sigma^s_{\alpha\beta}$ as the force conjugate to $g^s_{\alpha\beta}$ and h_α as the force conjugate to N_α, we can write, in the limit of weak flux, the following linear functions of the fluxes for the forces, which satisfy the symmetry properties of uniaxial nematics:

$$\begin{aligned}\sigma^s_{\alpha\beta} = {} & \rho_1\delta_{\alpha\beta}g^s_{\mu\mu} + \rho_2 n_\alpha n_\beta g^s_{\mu\mu} + \rho_3\delta_{\alpha\beta}n_\gamma n_\mu g^s_{\gamma\mu} + \alpha_1 n_\alpha n_\beta n_\mu n_\rho g^s_{\mu\rho} + \alpha_4 g^s_{\alpha\beta} \\ & + \tfrac{1}{2}(\alpha_5+\alpha_6)\left(n_\alpha n_\mu g^s_{\mu\beta} + n_\beta n_m u g^s_{\mu\alpha}\right) + \tfrac{1}{2}\gamma_2(n_\alpha N_\beta + n_\beta N_\alpha)\end{aligned} \tag{47}$$

$$h_\mu = \gamma_2' n_\alpha g^s_{\alpha\mu} + \gamma_1 N_\mu. \tag{48}$$

Note that all the coefficients ρ, α, γ have the dimensionality of viscosity, and the Onsager's symmetry of kinetic coefficients [47] implies that $\gamma_2' = \gamma_2$.

If the liquid is incompressible $\left(g^s_{\mu\mu} = 0\right)$, we arrive at the Leslie–Ericksen theory where the total viscous stress tensor reads

$$\sigma^{LE}_{\alpha\beta} = \alpha_1 n_\alpha n_\beta n_\rho n_\mu g^s_{\mu\rho} + \alpha_4 g^s_{\alpha\beta} + \alpha_5 n_\alpha n_\mu g^s_{\mu\beta} + \alpha_6 n_\beta n_\mu g^s_{\mu\alpha} + \alpha_2 n_\alpha N_\beta + \alpha_3 n_\beta N_\alpha, \tag{49}$$

where the viscosity constants $\alpha_1, \ldots, \alpha_6$ are called the Leslie coefficients. In the isotropic phase, all of them vanish except α_4, which becomes the isotropic shear viscosity coefficient η. They have to fulfil the Onsager reciprocity, which for a nematic is known as the Parodi relation [48], $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$. So effectively there are only five independent coefficients. Three of them are connected with the symmetric part of the stress tensor and the other two with the anti-symmetric part

$$\sigma^a_{\alpha\beta} = \frac{\gamma_1}{2}(n_\beta N_\alpha - n_\alpha N_\beta) + \frac{\gamma_2}{2}\left(n_\beta n_\mu g^s_{\mu\alpha} - n_\alpha n_\mu g^s_{\mu\beta}\right) \tag{50}$$

with

$$\gamma_1 = \alpha_3 - \alpha_2 \qquad \text{and} \qquad \gamma_2 = \alpha_2 + \alpha_3 \equiv \alpha_6 - \alpha_5. \tag{51}$$

The coefficients γ_1 and γ_2 determine the viscous torque acting on the molecule: γ_1 is characteristic of pure director rotations and γ_2 describes the contribution due to a shear flow. The equation of motion of the director reads

$$\boldsymbol{n} \times (\gamma_1 \boldsymbol{N} + \gamma_2 \boldsymbol{n} \cdot g^s) = 0. \tag{52}$$

If we assume undeformed director field, the conservation law for angular momentum can be neglected. If one would like to consider the case of a deformed system, the stress tensor and the conservation of angular momentum have to be modified, and equations (50) and (52) should be extended to a more general forms containing the additional elastic stress. Elastic stress induced by spatial inhomogeneities will be the subject of interest in section 6. The status of the LE equation as a constitutive equation for nematics is therefore analogous to that of the Newtonian constitutive equation as a description for ordinary liquid.

3.3. Microscopic stress tensor

In general, the transport coefficients can be obtained within the framework of classical kinetic theory [2, 3]. In this context, the macroscopic stress tensor can be defined as an ensemble average of σ^m_{ij}, the corresponding microscopic stress tensor, over the non-equilibrium distribution function $w\{\boldsymbol{x}_i\}$, where $\boldsymbol{x}_i$ are the relevant phase-space variables. In fact the microscopic stress tensor describes the evolution of the microscopic momentum density $\mathbf{p}(\boldsymbol{R})$ according to the local conservation law:

$$\frac{\mathrm{d}\mathbf{p}(\boldsymbol{R})}{\mathrm{d}t} = \nabla \cdot \sigma^m(\boldsymbol{R}). \tag{53}$$

The general expression for the microscopic stress tensor can be obtained with the help of the microscopic equations of motion for individual molecules. For a nematic fluid composed of rigid elongated particles, approximate expressions for the microscopic stress tensor had been given in the literature [19, 22]. Here we outline a careful derivation of the microscopic stress tensor for a general uniaxial molecule.

A molecule can be considered as a rigid body made up of bounded points of mass m_k. Then the total momentum in the system of many such particles is

$$\mathbf{p}(\boldsymbol{R}) = \sum_i \sum_k m_k \left[\boldsymbol{v}_i + (\boldsymbol{\omega}_i \times \boldsymbol{r}_{ik})\right] \delta(\boldsymbol{R} - \boldsymbol{r}_i - \boldsymbol{r}_{ik}) \tag{54}$$

where the index i indicates a molecule and k a point inside the molecule, see figure 3. Here $\boldsymbol{\omega}_i$ is the angular velocity of rigid molecular rotation and $\boldsymbol{v}_i$ the velocity of its centre of mass (COM). $\boldsymbol{r}_i$ is the position of the COM in the laboratory frame, while $\boldsymbol{r}_{ik}$ is the position of the point k in the molecular frame so that the velocity of a point k of the ith molecule in the laboratory frame is $\boldsymbol{v}_{ik} = \boldsymbol{v}_i + \boldsymbol{\omega}_i \times \boldsymbol{r}_{ik}$.

Formally expanding the delta-function in powers of $\boldsymbol{r}_{ik}$, we have

$$\delta(\boldsymbol{R} - \boldsymbol{r}_i - \boldsymbol{r}_{ik}) = \delta(\boldsymbol{R} - \boldsymbol{r}_i) - \boldsymbol{r}_{ik} \cdot \nabla_R \delta(\boldsymbol{R} - \boldsymbol{r}_i) + f(\nabla^2 \delta) + \cdots. \tag{55}$$

Taking the time derivative in equation (54) and substituting equation (55) into (53), while working in the linear flow regime where higher order terms $\nabla^2\delta$ can be neglected, we find that the microscopic stress tensor can be separated into the translational (a function of $\boldsymbol{r}_i$ and its derivatives) and orientational parts. Comparing these terms with the $\nabla \cdot \sigma^m(\boldsymbol{R})$ on the right-hand side of definition (53) we obtain the orientational part of the microscopic stress tensor:

$$\begin{aligned}\sigma^{\mathrm{or}}_{\alpha\beta} = {} & \sum_i \sum_k m_k \left[\boldsymbol{\omega}_i \times (\boldsymbol{\omega}_i \times \boldsymbol{r}_{ik}) + \dot{\boldsymbol{\omega}}_i \times \boldsymbol{r}_{ik}\right]_\alpha (\boldsymbol{r}_{ik})_\beta \delta(\boldsymbol{R} - \boldsymbol{r}_i) \\ & + \sum_i \sum_k m_k (\boldsymbol{\omega}_i \times \boldsymbol{r}_{ik})_\alpha (\boldsymbol{\omega}_i \times \boldsymbol{r}_{ik})_\beta \delta(\boldsymbol{R} - \boldsymbol{r}_i).\end{aligned} \tag{56}$$

The translational part of the microscopic stress would determine the isotropic viscosity, arising from non-equilibrium pair correlations in liquid. Its contribution will remain in the nematic phase as well, adding a significant constant to the Leslie coefficient α_4, a fact often overlooked in molecular theories of nematic viscosity.

Expanding the tensors in (56) and grouping together the expressions for the inertia tensor of rigid body rotating about its COM, defined as

$$I_{\alpha\beta} = \sum_k m_k (r^2 \delta_{\alpha\beta} - r_\alpha r_\beta), \tag{57}$$

we can rewrite the orientational part of microscopic stress tensor as a sum over all molecules i:

$$\begin{aligned}\sigma^{\mathrm{or}}_{\alpha\beta} = {} & -\sum_i [I_{\alpha\delta}(I^{-1})_{\nu l} \Gamma^l \epsilon_{\beta\nu\delta} + I_{mk} \epsilon_{\alpha l m} \omega_l \epsilon_{\beta j k} \omega_j + I_{\alpha\nu} \omega_\beta \omega_\nu - I_{\alpha\beta} \omega^2] \delta(\boldsymbol{R} - \boldsymbol{r}_i) \\ & + \sum_i \epsilon_{\beta\nu\alpha} (I^{-1})_{\nu l} \Gamma^l \left(\frac{1}{2} \mathrm{Tr}(I_{\alpha\beta})\right) \delta(\boldsymbol{R} - \boldsymbol{r}_i).\end{aligned} \tag{58}$$

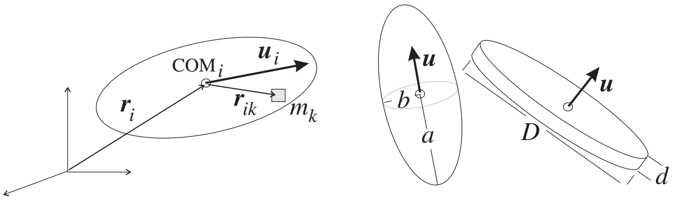

Figure 3. The molecule i (arbitrarily represented here as an ellipsoid, without loss of generality) has its centre-of-mass coordinate $\boldsymbol{r}_i$ in the laboratory frame. In the frame of its COM, the position of a given mass element m_k is $\boldsymbol{r}_{ik}$. The unit vector $\boldsymbol{u}_i$ represents the principal axis of the tensor of inertia moments of this molecule. For a uniaxial body, this tensor is equal to $I_{\alpha\beta} = I_\perp\delta_{\alpha\beta} + (I_\parallel - I_\perp)u_\alpha u_\beta$.

Here Γ_i is the total moment of the force acting on the ith molecule, arising from the dynamical relation $\Gamma_i = I_{ij}\dot{\omega}_j$. The torque acting on the molecule i from all its neighbours is given by the rotational gradient of the pair potential,

$$\Gamma_\alpha(r^i) = -\sum_j \epsilon_{\alpha\beta\gamma} u^i_\beta \frac{\partial U(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{r}_{ij})}{\partial u^i_\gamma}, \tag{59}$$

where $U(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{r}_{ij})$ is the interaction potential for molecules i and j. Since all variables in (59) are related to the particle i, summing over the rest of the particles gives, by definition, the molecular field (often called the mean-field potential)

$$U(\boldsymbol{u}_i, \boldsymbol{r}_i) = \sum_j U(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{r}_{ij}). \tag{60}$$

Section 5.3 gives more detail to these concepts. For a rigid uniaxial molecule, we should define the principal molecular frame in which the inertial tensor is diagonal with components $I_\perp$ and $I_\parallel$ (see figure 3):

$$I_{\alpha\beta} = I_\perp\delta_{\alpha\beta} + (I_\parallel - I_\perp)u_\alpha u_\beta. \tag{61}$$

Substituting equations (59) and (61) into (58), we finally have

$$\begin{aligned}\sigma^{\rm or}_{\alpha\beta} = \sum_i &\left[\left(1 - \frac{I_\parallel}{2I_\perp}\right)u_\alpha\frac{\partial U}{\partial u_\beta} - \frac{I_\parallel}{2I_\perp}u_\beta\frac{\partial U}{\partial u_\alpha} + \left(\frac{I_\parallel - I_\perp}{I_\perp}\right)u_\alpha u_\beta u_m\frac{\partial U}{\partial u_m}\right]\delta(\boldsymbol{R} - \boldsymbol{r}_i)\\ &- \sum_i (I_\parallel - I_\perp)[(\boldsymbol{\omega}\times\boldsymbol{u})_\alpha(\boldsymbol{\omega}\times\boldsymbol{u})_\beta + u_\alpha u_\nu\omega_\nu\omega_\beta - \omega^2 u_\alpha u_\beta]\delta(\boldsymbol{R} - \boldsymbol{r}_i)\end{aligned} \tag{62}$$

Here the two groups of terms are deliberately assembled in the way to highlight the distinction between the potential and the kinetic contributions to the microscopic stress tensor. For an ellipsoid, with semi-axes a and width b (see figure 3) the moments of inertia along and perpendicular to the director are $I_\parallel = \frac{2}{5}Mb^2$ and $I_\perp = \frac{1}{5}M(a^2 + b^2)$, with M the total mass of the molecule. For a long thin 'rod-like' particle $p = a/b \gg 1$ and $I_\parallel \ll I_\perp$; for an oblate ellipsoid with $b \gg a$ they are of the same order of magnitude. (Later in this text we shall be dealing with thin flat discs, with thickness d and diameter $D \gg d$, which have $I_\parallel = \frac{1}{8}MD^2$ and $I_\perp = \frac{1}{4}M(\frac{1}{3}d^2 + \frac{1}{4}D^2)$, also of the same order of magnitude.) Substituting the I-values for an ellipsoid into equation (62) gives the final form:

$$\begin{aligned}\sigma^{\rm or}_{\alpha\beta} = \sum_i &\left[\frac{p^2}{p^2+1}u_\alpha\frac{\partial U}{\partial u_\beta} - \frac{1}{(p^2+1)}u_\beta\frac{\partial U}{\partial u_\alpha} - \frac{p^2-1}{p^2+1}u_\alpha u_\beta u_m\frac{\partial U}{\partial u_m}\right]\delta(\boldsymbol{R} - \boldsymbol{r}_i)\\ &+ \sum_i \frac{p^2-1}{p^2+1}I_\perp[(\boldsymbol{\omega}\times\boldsymbol{u})_\alpha(\boldsymbol{\omega}\times\boldsymbol{u})_\beta + u_\alpha u_\nu\omega_\nu\omega_\beta - \omega^2 u_\alpha u_\beta]\delta(\boldsymbol{R} - \boldsymbol{r}_i)\end{aligned} \tag{63}$$

with the molecular aspect ratio $p = a/b$.

The macroscopic continuum stress tensor is obtained by statistical averaging of (63) which implies the integration over the angles ($\boldsymbol{u}$) and angular velocity ($\boldsymbol{\omega}$) with a proper distribution function. The averaging over the velocity can be easily performed since it is determined by the one-particle local Maxwell distribution function $= \exp[-I_\perp(\boldsymbol{\omega} - \boldsymbol{\omega}_{\mathrm{res}})^2/2kT]$, where $\boldsymbol{\omega}_{\mathrm{res}}$ is the background angular velocity due to flow. The second term on the right-hand side of equation (63) therefore gives, after averaging, the 'kinetic' part of the stress tensor.

The stress tensor in terms of microscopic orientational variables, but not molecular velocities (which have just been averaged out as fast variables), takes the form

$$\sigma^{\mathrm{or}}_{\alpha\beta} = \sum_i \left\{ 3kT\,\tilde{p}\left(u_\alpha u_\beta - \frac{1}{3}\delta_{\alpha\beta}\right) + \frac{p^2}{p^2+1}u_\alpha \frac{\partial U}{\partial u_\beta} - \frac{1}{p^2+1}u_\beta \frac{\partial U}{\partial u_\alpha} \right.$$
$$\left. - \frac{p^2-1}{p^2+1}u_\alpha u_\beta u_m \frac{\partial U}{\partial u_m}\right\}\delta(\boldsymbol{R} - \boldsymbol{r}_i) \qquad (64)$$

where $\tilde{p} = (p^2 - 1)(p^2 + 1)$ is often called the form factor of the molecules. Note that the assumption made about ellipsoidal shape of the anisotropic molecule, leading to the particular expressions for $I_\parallel$ and $I_\perp$ and the resulting form of (64), was not necessary at all. The theory of microscopic stress at the level of (62) or (58) is totally general for rigid uniaxial particles.

The separation of the orientational part of stress tensor into two parts, kinetic and potential, has an important physical significance. The kinetic part, proportional to $3kT$, represents the momentum flux due to the translation of individual molecules, while the second, potential part, represents the flux arising from intermolecular forces. Both are referred to a coordinate system moving with the local fluid velocity $\boldsymbol{v}$. In a dilute gas of molecules, the kinetic part gives the dominant contribution [23], while in a dense fluid, the orientational motion is inhibited and the potential part gives the dominant contribution. In the following sections, we will assume that the system has uniform density and the summation over the delta-functions is replaced by a constant number density $\rho(\boldsymbol{R})$.

3.4. Preliminary discussion points

It is obvious that in the limit $p \to \infty$, equation (64) reduces to the familiar results for long rods system obtained previously [19, 22]. For the disc-like molecules the result is of special interest. Since in this case the form factor $\tilde{p}$ is negative, one may expect a change in sign of certain viscosity coefficients. One can speculate that more drastic differences in viscosity coefficients will arise from consideration of more precise mean-field potential.

It is interesting to compare these expressions with classical results of Kuzuu and Doi [19]. In their approach, the elastic stress tensor is obtained by relating changes in free energy to the elastic stress and virtual deformation [23]. They implicitly assumed that such free energy can be defined even in non-equilibrium state since the system behaves as an elastic material for instantaneous deformation. By making this approximation, they obtained the stress tensor:

$$\sigma_{\alpha\beta} = \tilde{p}\left[3\rho kT\left\langle u_\alpha u_\beta - \tfrac{1}{3}\delta_{\alpha\beta}\right\rangle - \rho\langle u_\alpha(\boldsymbol{u}\times\boldsymbol{\partial}U)_\beta\rangle\right]. \qquad (65)$$

This agrees with (64) in the kinetic part of the stress tensor, but not in the potential-dependent part. In fact if one uses the free-energy approach, following Kuzuu and Doi, one finds that the expression they had derived contains only the symmetric part of our complete microscopic stress tensor. As a result, they had to introduce arbitrary magnetic field to generate asymmetric torque contribution, which however exists in nematics even in the absence of magnetic field. In this respect, our results give a more accurate description since equation (64) can be antisymmetrized, without imposing external conditions to the system.

A cautionary remark has to be made. We have assumed uniform liquid concentration throughout the sample. In reality, a phase separation may occur between the isotropic and nematic phases with different concentrations, as often is the case in lyotropic systems. The kinetic equation will describe the internal dynamics in each of the phases, which is thermodynamically stable. It is however not sufficient to describe the hydrodynamics of the nematics near phase separation boundary. This fact must be borne in mind while comparing the theory with experiments in the bi-phase region.

4. Microscopic viscosity coefficients

In this section, we put together results from sections 2 and 3 to derive a set of the microscopic expressions for the Leslie coefficients. We also investigate the effects of nonlinear corrections due to gyroscopic motions in discotic nematics. These effects give no corrections to the Miesowicz viscosities but generate a nonlinear rotational viscosity γ' that depends on the aspect ratio p and the longitudinal moment of inertia $I_{\parallel}$.

The motivation for finding the microscopic expressions for the Leslie coefficients relies on the concept that the macroscopic continuum stress tensor is a result of averaging its microscopic equivalent σ^m over the appropriate *non-equilibrium* distribution function. The underlying assumption is that the nematic liquid crystal performs rotational Brownian motion in a mean-field potential and whose orientational distribution function satisfies the kinetic equation (section 2). However, we note that the solution to the kinetic equation is non-trivial, even if one neglects the nonlinear terms (though of course it can be done via eigenfunction expansion method when the flow term is neglected). Instead, we demonstrate how, by following the approach used by Doi and others [19, 22], one can separate the macroscopic stress tensor into the symmetric and anti-symmetric parts, the microscopic viscosity coefficients can be obtained in a more elegant fashion.

4.1. Symmetric stress tensor

From equation (49), the symmetric stress tensor of the LE phenomenological theory can be written as

$$\sigma^s_{\alpha\beta} = \alpha_1 n_\alpha n_\beta n_\rho n_\mu g^s_{\mu\rho} + \alpha_4 g^s_{\alpha\beta} + \tfrac{1}{2}(\alpha_5+\alpha_6)\big(n_\alpha n_\mu g^s_{\mu\beta} + n_\beta n_\mu g^s_{\mu\alpha}\big) + \tfrac{1}{2}(\alpha_2+\alpha_3)(n_\alpha N_\beta + n_\beta N_\alpha) \tag{66}$$

where $g^s_{\alpha\beta}$ is the symmetric velocity gradient and $\boldsymbol{N}$ is the rate of angular rotation (46). Our aim is to derive a microscopic expression of the Leslie's viscosity coefficients from microscopic variables through a series of coarse-graining. The symmetric stress tensor can be obtained by averaging the microscopic stress tensor in equation (64) over the non-equilibrium distribution function,

$$\sigma^s_{ij} = \rho\big\langle 3kT\tilde{p}\big(u_i u_j - \tfrac{1}{3}\delta_{ij}\big) + \tfrac{1}{2}\tilde{p}(u_i\partial_j U + u_j\partial_i U - 2u_i u_j u_m \partial_m U)\big\rangle \tag{67}$$

where ρ is the number density of the nematic liquid crystal. $\langle\cdots\rangle$ denotes the average over the non-equilibrium single-particle orientation distribution function $\langle\cdots\rangle = \int w(\boldsymbol{u},t)\cdots \mathrm{d}\boldsymbol{u}$. Obviously, averaging with $w_{eq}(\boldsymbol{u})$ alone will return zero.

We next use a trick, in this context often attributed to Doi [19]. We consider the kinetic equation, obtained in section 2 and neglect higher order nonlinear terms,

$$\dot{w} + \alpha\partial_k(\Omega_k w) = \alpha^2\partial_k\left(\partial_k w + \frac{\partial_k U}{kT}w\right). \tag{68}$$

Multiplying this equation by a factor $\left(u_i u_j - \frac{1}{3}\delta_{ij}\right)$ and integrating over the director orientation making use of the orientational version of integration by parts: $\int \mathrm{d}\boldsymbol{u} A(\boldsymbol{u}) \boldsymbol{\partial} B(\boldsymbol{u}) = -\int \mathrm{d}\boldsymbol{u}\, [\boldsymbol{\partial} A(\boldsymbol{u})]\, B(\boldsymbol{u})$, we derive the following expressions for the four terms in (68):

$$\int \dot{w} \left(u_i u_j - \frac{1}{3}\delta_{ij}\right) \mathrm{d}\boldsymbol{u} = \frac{\partial}{\partial t}\left\langle u_i u_j - \frac{1}{3}\delta_{ij}\right\rangle \tag{69}$$

$$\begin{aligned}\int \partial_k(\Omega_k w) \left(u_i u_j - \frac{1}{3}\delta_{ij}\right) \mathrm{d}\boldsymbol{u} = &-\frac{1}{2}\left[g^a_{i\alpha}\langle u_\alpha u_j\rangle - g^a_{\alpha j}\langle u_\alpha u_i\rangle\right] \\ &+ \frac{\tilde{p}}{2}\left[2g^s_{\alpha\beta}\langle u_\alpha u_\beta u_i u_j\rangle - g^s_{\gamma i}\langle u_\gamma u_j\rangle - g^s_{\gamma j}\langle u_\gamma u_i\rangle\right]\end{aligned} \tag{70}$$

$$\int \partial_k(\partial_k w) \left(u_i u_j - \frac{1}{3}\delta_{ij}\right) \mathrm{d}\boldsymbol{u} = -6\left\langle u_i u_j - \frac{1}{3}\delta_{ij}\right\rangle \tag{71}$$

$$\int \partial_k \frac{(w\partial_k U)}{kT} \left(u_i u_j - \frac{1}{3}\delta_{ij}\right) \mathrm{d}\boldsymbol{u} = -\frac{1}{kT}\langle u_i\partial_j U + u_j\partial_i U - 2u_i u_j u_m \partial_m U\rangle. \tag{72}$$

Combining these results, equation (68) after averaging gives

$$\frac{\partial Q_{ij}}{\partial t} = F_{ij} + G_{ij} \tag{73}$$

where

$$Q_{ij} = \left\langle u_i u_j - \frac{1}{3}\delta_{ij}\right\rangle \tag{74}$$

$$F_{ij} = -6\alpha^2\left\langle u_i u_j - \frac{1}{3}\delta_{ij}\right\rangle - \frac{\alpha^2}{kT}\langle u_i\partial_j U + u_j\partial_i U - 2u_i u_j u_m \partial_m U\rangle \tag{75}$$

$$G_{ij} = -\frac{1}{2}\alpha\tilde{p}\left[2g^s_{\alpha\beta}\langle u_\alpha u_\beta u_i u_j\rangle - g^s_{\gamma i}\langle u_\gamma u_j\rangle - \langle u_\gamma u_i\rangle g^s_{\gamma j}\right] + \frac{\alpha}{2}\left[g^a_{i\alpha}\langle u_\alpha u_j\rangle - \langle u_\alpha u_i\rangle g^a_{\alpha j}\right]. \tag{76}$$

Following this, the symmetric part of the macroscopic stress tensor can be written as

$$\begin{aligned}\sigma^s_{ij} &= \rho\left\langle 3kT\tilde{p}\left(u_i u_j - \frac{1}{3}\delta_{ij}\right) + \frac{\tilde{p}}{2}\left(u_i\frac{\partial U}{\partial u_j} + u_j\frac{\partial U}{\partial u_i} - 2u_i u_j u_m\frac{\partial U}{\partial u_m}\right)\right\rangle \\ &\equiv -\rho\frac{kT}{2\alpha^2}\tilde{p}F_{ij} = -\rho\frac{kT}{2\alpha^2}\tilde{p}\left[\frac{\partial Q_{ij}}{\partial t} - G_{ij}\right] \\ &= \rho\frac{kT\tilde{p}^2}{4\alpha}\left[-2g^s_{\alpha\beta}\langle u_\alpha u_\beta u_i u_j\rangle + \langle u_\gamma u_j\rangle g^s_{\gamma i} + \langle u_\gamma u_i\rangle g^s_{\gamma j}\right] \\ &\quad + \rho\frac{kT\tilde{p}}{4\alpha}\left[\langle u_\alpha u_j\rangle g^a_{i\alpha} - \langle u_\alpha u_i\rangle g^a_{\alpha j}\right] - \rho\frac{kT\tilde{p}}{2\alpha^2}\frac{\partial}{\partial t}\langle u_i u_j\rangle.\end{aligned} \tag{77}$$

The various moments of orientational distribution function can be expressed generally in terms of the macroscopic average director field $\boldsymbol{n}$ and the delta-functions which must obey the directors symmetries that $\boldsymbol{n}$ and $-\boldsymbol{n}$ are equivalent. The derivation of the various moments is straightforward and we simply quote the results:

$$\langle u_i u_j\rangle = S_2 n_i n_j + \tfrac{1}{3}(1 - S_2)\delta_{ij} \tag{78}$$

$$\begin{aligned}\langle u_\alpha u_\beta u_i u_j\rangle = &S_4 n_\alpha n_\beta n_i n_j + \tfrac{1}{15}\left(1 - \tfrac{10}{7}S_2 + \tfrac{3}{7}S_4\right)(\delta_{\alpha\beta}\delta_{ij} + \delta_{\alpha i}\delta_{\beta j} + \delta_{\alpha j}\delta_{\beta i}) + \tfrac{1}{7}(S_2 - S_4) \\ &\times (n_\alpha n_\beta\delta_{ij} + n_i n_j\delta_{\alpha\beta} + n_i n_\alpha\delta_{j\beta} + n_i n_\beta\delta_{\alpha j} + n_j n_\alpha\delta_{\beta i} + n_j n_\beta\delta_{i\alpha})\end{aligned} \tag{79}$$

where S_2 and S_4 are the scalar order parameters corresponding to the averaged second and fourth Legendre's polynomials of molecular orientation. The main scalar order parameter can be derived from the order parameter tensor S_{ij}:

$$S_{ij} = \left\langle u_i u_j - \tfrac{1}{3}\delta_{ij}\right\rangle = S_2\left(n_i n_j - \tfrac{1}{3}\delta_{ij}\right). \tag{80}$$

Multiplying $n_i n_j$ to equation (80) gives $S_2 = \frac{3}{2}\left\langle(\boldsymbol{n}\cdot\boldsymbol{u})^2 - \frac{1}{3}\right\rangle$. Thus S_2 is a scalar measure of how perfectly the molecules are oriented along $\boldsymbol{n}$. The expression for S_4 is derived in the same way.

Substituting the average moments we eventually obtain the desired expression of σ^s_{ij} in terms of velocity gradient and the directors,

$$\begin{aligned}\sigma^s_{ij} = \frac{kT\tilde{p}^2}{4\alpha}\rho\Bigg[&-2S_4 n_\alpha n_\beta n_i n_j g^s_{\alpha\beta} + \frac{2}{35}(7 - 5S_2 - 2S_4)g^s_{ij}\\ &+ \frac{1}{7}(3S_2 + 4S_4)\left(n_i n_\alpha g^s_{\alpha j} + n_j n_\beta g^s_{\beta j}\right) - \frac{2}{7}(S_2 - S_4)n_\alpha n_\beta g^s_{\alpha\beta}\delta_{ij}\Bigg]\\ &- \frac{kT\tilde{p}S_2}{4\alpha}\rho\left[n_i\left(\frac{\dot{n}_j}{\alpha} - g^a_{j\alpha}n_\alpha\right) + n_j\left(\frac{\dot{n}_i}{\alpha} - g^a_{i\alpha}n_\alpha\right)\right].\end{aligned} \tag{81}$$

The term $n_\alpha n_\beta g^s_{\alpha\beta}\delta_{ij}$ contributes to the scalar pressure, which therefore does not appear in the LE stress tensor. Comparing with equation (66), we find the corresponding Leslie viscosity coefficient combinations, after restoring to dimensional forms:

$$\alpha_1 = -\rho\lambda_\perp\tilde{p}^2 S_4 \tag{82}$$

$$\alpha_2 + \alpha_3 = -\rho\lambda_\perp\tilde{p}S_2 \tag{83}$$

$$\alpha_4 = \frac{\rho\lambda_\perp}{35}\tilde{p}^2(7 - 5S_2 - 2S_4) \tag{84}$$

$$\alpha_5 + \alpha_6 = \frac{\rho\lambda_\perp}{7}\tilde{p}^2(3S_2 + 4S_4). \tag{85}$$

This gives four out of five required relations; the main rotational viscosity coefficient $\gamma_1 = \alpha_2 - \alpha_3$ has to be determined from the antisymmetric analysis of torques.

4.2. Anti-symmetric stress tensor

For an isotropic liquid, the stress tensor must be a symmetric function due to the demand on the local balance of torques. For anisotropic nematics, we expect the anisotropic part of the stress tensor to be non-vanishing due to the orientational torques of the director. The existence of a viscous stress in the fluid has to be a result of averaging over the non-equilibrium distribution function. We can write the non-equilibrium distribution function as $w = w_0(1 + h[\boldsymbol{u}])$ where h represents the deviation from the equilibrium distribution function w_0 (or w_{eq}) which in turn can be written in a very general form that reflects the symmetries of the terms in LE theory. The macroscopic antisymmetric stress tensor then takes the form

$$\sigma^a_{\alpha\beta} = \frac{\rho}{2}\int\left(u_\alpha\frac{\partial U}{\partial u_\beta} - u_\beta\frac{\partial U}{\partial u_\alpha}\right)w_0[\boldsymbol{u}]h[\boldsymbol{u}]\,\mathrm{d}\boldsymbol{u} \tag{86}$$

where the antisymmetric microscopic stress tensor follows from taking the antisymmetric part of (64). The antisymmetric stress tensor obtained this way has to be equivalent to that obtained in the phenomenological LE formalism.

In this case, there is no straightforward trick to solve $\sigma^a_{\alpha\beta}$, as was previously done for $\sigma^s_{\alpha\beta}$. Instead we have to solve the kinetic equation (68) to determine $h[\boldsymbol{u}]$ uniquely. The phenomenological antisymmetric stress tensor is given by equation (50), which suggests that γ_1 is related to the rotation of the director $\dot{\boldsymbol{n}}$ and the flow vorticity $(\nabla \times \boldsymbol{v})$. Therefore we have the freedom to choose the nematic system in zero flow $(\boldsymbol{\Omega} = 0)$ such that the solution of the kinetic equation gives h which is flow-independent and can be equated to the γ_1 term. The kinetic equation becomes

$$\dot{w} = \alpha^2 \partial_\beta \left[\partial_\beta w + \frac{\partial_\beta U}{kT} w \right] = \alpha^2 w_0 \left[\partial^2 h - \frac{\partial_\beta U}{kT} \partial_\beta h \right]. \tag{87}$$

Assuming the mean-field potential to be of the Maier–Saupe form [43]

$$U(\theta) = -JS_2 \left[\frac{3}{2} (\boldsymbol{n} \cdot \boldsymbol{u})^2 - \frac{1}{2} \right], \tag{88}$$

and the equilibrium orientational distribution $w_0 \propto \exp[-U/kT]$, the equation (87) becomes

$$\partial^2 h - \frac{\partial_\beta U}{kT} \partial_\beta h \simeq \frac{3J_o S_2}{\alpha^2 kT} (\boldsymbol{n} \cdot \boldsymbol{u})(\dot{\boldsymbol{n}} \cdot \boldsymbol{u})(1 + h). \tag{89}$$

As designed, the only source of deviation from equilibrium here is the time dependence of the uniformly rotating director. We have assumed that the term $\boldsymbol{n} \cdot \dot{\boldsymbol{u}}$ is negligibly small for a nematic system approaching quasi-static state such that all molecules are almost aligned parallel to the averaged director $\boldsymbol{n}$. An equivalent argument is that $\boldsymbol{n} \cdot \dot{\boldsymbol{u}}$ is proportional to the angular velocity which is a fast dynamical variable that had been previously integrated out to yield the kinetic equation (68) in terms of $w(\boldsymbol{u}, t)$.

Symmetry of the problem suggests the following expression for the linear non-equilibrium correction h,

$$h = h_o (\boldsymbol{n} \cdot \boldsymbol{u})(\dot{\boldsymbol{n}} \cdot \boldsymbol{u}) \tag{90}$$

where h_o is a constant to be determined self-consistently. In this respect, we can neglect h on the right-hand side of equation (89) since it produces nonlinear terms. Substituting (90) into equation (89) determines h_o (in its dimensional form):

$$h_o = -\frac{\lambda_\perp}{kT} \frac{JS_2/kT}{2 + JS_2/kT} \tag{91}$$

where the ratio $q = JS_2/kT$ denotes the strength of the nematic order and $\lambda_\perp$ is the rotational friction constant. Substituting this result into equation (86) and manipulating in spherical coordinates, we finally obtain the averaged antisymmetric stress tensor with the explicit coefficient in front

$$\sigma^a_{\alpha\beta} = \frac{1}{70} \frac{(JS_2/kT)^2}{2 + JS_2/kT} \lambda_\perp \rho (7 + 5S_2 - 12S_4)(n_\alpha \dot{n}_\beta - \dot{n}_\alpha n_\beta). \tag{92}$$

Comparing with the continuum theory definition in equation (49) we identify that

$$\gamma_1 = \alpha_3 - \alpha_2 = \frac{1}{35} \frac{(JS_2/kT)^2}{2 + (JS_2/kT)} \lambda_\perp \rho (7 + 5S_2 - 12S_4), \tag{93}$$

which has the required property of vanishing when S_2 goes to zero. Making use of equations (82)–(85), we have the following microscopic expressions for the remaining Leslie coefficients:

$$\alpha_2 = -\frac{1}{2} (\rho \lambda_\perp \tilde{p} S_2 + \gamma_1) \tag{94}$$

$$\alpha_3 = -\frac{1}{2} (\rho \lambda_\perp \tilde{p} S_2 - \gamma_1) \tag{95}$$

$$\alpha_5 = \frac{1}{2}\rho\lambda_\perp\tilde{p}\left[S_2 + \frac{\tilde{p}}{7}(3S_2 + 4S_4)\right] \tag{96}$$

$$\alpha_6 = \frac{1}{2}\rho\lambda_\perp\tilde{p}\left[-S_2 + \frac{\tilde{p}}{7}(3S_2 + 4S_4)\right]. \tag{97}$$

The above analysis leads to the following theoretical predictions.

(1) The microscopic expressions for the viscosity coefficients depend strongly on the order parameters and on the alignment of the director in the fluid. They also depend explicitly on the geometrical shape of the spheroid which manifest itself in the form factor $\tilde{p}$. Since the order parameters are the averaged property, the Leslie coefficients do not depend explicitly on the exact form of the nematic potential U. Instead, the intermolecular potential determines uniquely the rotational friction constant $\lambda_\perp$ (see section 5).

(2) In the above analysis, we have paid particular attention to the fact that the general symmetric part of the microscopic stress tensor for a spheroid must be enriched with the form factor $\frac{p^2-1}{p^2+1}$, in contrast to previous works which treated only long-rods nematics [19, 22]. This allows us to take p to be asymptotically zero for the case of a discotic nematic, in which case the form factor $\tilde{p}$ goes to -1. This implies a change in the signs of certain viscosity coefficients, like α_5 and α_6. In the limit of small γ_1, both α_2 and α_3 are large and positive for a discotic nematic, but are negative for rod-like nematics. This is in accordance with earlier theoretical predictions [8, 11].

(3) The geometrical shape appears to have no effects on the value of α_4. In the LE formalism, this term accounts for the Newtonian behaviour which is present in isotropic liquid too. It accounts phenomenologically for contributions to momentum transport other than those due to rotational motions. For spherically symmetric molecules, this will be the sole contribution towards the viscosity of the liquid, mostly determined by the translational molecular degrees of freedom, which we have not considered here at all. In the nematic case, according to equation (85), the orientational part of α_4 vanishes in the limit of strong order when S_2 and S_4 tend to be 1. This corresponds to the fact that as the liquid approaches its full nematic alignment, its isotropic counterpart, independent of the shape of the anisotropic molecules, ceases to exist and so is α_4. This suggests that α_4 consists of two independent contributions: the isotropic α_4^{iso} which denotes contributions from momentum transport, in the style of classical works of Kirkwood and others [1–3], and the additional contribution α_4^{nem}, which we derived above.

(4) From equation (93), we see that as the intermolecular coupling strength q increases, the rotational viscosity γ_1 increases significantly, leading to large energy dissipation for uniform director rotation with respect to the matrix. This suggests that γ_1 characterizes director rotation that is associated with overcoming the potential barrier which is dictated by the order parameter S_2. A strong nematic potential therefore increases the viscous loss.

(5) There is an alternative approach towards evaluating the antisymmetric stress tensor, by taking the steady-state solution $\dot{w} = 0$ in the kinetic equation, instead of the zero flow condition $\boldsymbol{\Omega} = 0$ as we have done. In this case, we are looking for the flow-dependent terms of $\sigma^a_{\alpha\beta}$ which will eventually give us values of γ_1 and γ_2 [22, 49]. This method bypasses some of the approximations in the calculation above, but gives similar expression of γ_1. We do not include such an alternative derivation here.

4.3. Reactive coefficient and director tumbling

We next discuss how an understanding of γ_1 and γ_2 leads to a description of non-trivial dynamics such as director tumbling. The ratio of the negative of the irrotational torque coefficient γ_2 over the rotational viscosity γ_1 is often known as the reactive coefficient or *tumbling parameter* [43]. Here 'reactive' means that the term is reversible, i.e. no sign changes in time-reversal and non-dissipative hence producing no dissipation either going forwards or backwards in time. This parameter represents the competing effects of strain to vorticity torques acting on the director $\boldsymbol{n}$. Our results from previous section give for this parameter, which is defined as the negative ratio of the two rotational viscosities:

$$-\frac{\gamma_2}{\gamma_1} = \frac{1+\alpha_3/\alpha_2}{1-\alpha_3/\alpha_2} = \tilde{p}\frac{35S_2}{7+5S_2-12S_4}\frac{2+JS_2/kT}{(JS_2/kT)^2}. \tag{98}$$

The form factor $\tilde{p}$ contributes to a sign inversion for γ_2/γ_1 between discotic and rod-like nematics. For long rods, $\tilde{p}$ goes to 1, $\alpha_3/\alpha_2 < 1$ and $-\gamma_2/\gamma_1 > 1$. For disc-like molecules, $\tilde{p}$ goes to -1, $\alpha_3/\alpha_2 > 1$, and $-\gamma_2/\gamma_1 < -1$. This conclusion agrees well with the analytic solutions obtained via Poisson bracket formalism of Volovik [8].

In a more quantitative manner, we can consider the time evolution of $\boldsymbol{n}$. This can be obtained from the conservation of angular momentum in the LE theory [13, 50]:

$$\frac{\partial \boldsymbol{n}_i}{\partial t} = (\boldsymbol{\nu}\times\boldsymbol{n})_i - \frac{\gamma_2}{\gamma_1}[(g^s\cdot\boldsymbol{n})_i - (\boldsymbol{n}\cdot g^s\cdot\boldsymbol{n})n_i] \tag{99}$$

where as before, g^s is the symmetric velocity gradient, $\boldsymbol{\nu}$ is the vorticity defined in equation (46) and the reactive coefficient is a factor in the second term. From (99) it is apparent that for $|\gamma_2/\gamma_1| > 1$, the straining motion dominates and the director tends towards a steady-state orientation angle θ relative to the stream lines, when the hydrodynamic torque $\boldsymbol{\Gamma}$ vanishes [6, 11]:

$$\tan\theta = \sqrt{\frac{\gamma_2+\gamma_1}{\gamma_2-\gamma_1}} = \sqrt{\frac{\alpha_3}{\alpha_2}}. \tag{100}$$

θ is called the *flow alignment angle*, defined as the angle between the director axis and the flow in the state of balanced nematic and viscous torques. We see that the straining term can be interpreted as the $\rho\lambda_\perp S_2$ term which is dictated by the rotational friction and the order parameter strength, while γ_1 dictates the vorticity effects. Steady-state alignments occur when shearing rotates the molecules until they are almost parallel or perpendicular to the flow direction and at this orientation they cease to rotate. As we had seen, for rod-like nematic, $\alpha_3/\alpha_2 < 1$, equation (100) states that $\theta < 45^\circ$. In fact the rods align their axes almost parallel to the flow direction. For the discotic nematic, we have the opposite situation when $\alpha_3/\alpha_2 \gg 1$, and $\theta \approx 90^\circ$. The discs therefore tend to align with their axes perpendicular to the flow direction, with one of the long axes of the discs being parallel to the flow direction. The other long axis seems to point in the gradient direction, so that the director orients in the vorticity direction. Such behaviour has indeed been observed in scattering studies [24], and agrees with earlier predictions [11].

Equation (99) also suggests that when $|\gamma_2/\gamma_1| < 1$, the vorticity term dominates over the straining motion and the director can no longer find a steady-state orientation. This is reflected in $\gamma_1 \gg \rho\lambda_\perp S_2$ and $\alpha_3/\alpha_2 < 0$. As a result no alignment angle can be established. In this situation, the molecules deviate significantly from the average orientation, and even if the director is almost aligned with the flow field, there is a net torque on molecules that are not perfectly aligned with the field. Due to the anisotropic shape and the pair potential, the torque on any one molecule is transmitted to the others and the whole assembly of molecules continues rotating even at the instant the average direction is parallel to the flow. The nematics therefore do not have a preferred alignment angle, and at any orientation angle, the director experiences a viscous torque tending to rotate it. This leads to the tumbling phenomenon. The steady shear-flow properties of tumbling nematics are very different from those of flow-aligning nematics [51, 52], and the effects of tumbling and its arrest are believed to lead to observed transitions of normal stress differences from positive to negative values [50].

In this section, we discussed several predictions of the LE theory pertaining to the tumbling of the director. However we note that these results do not immediately apply to real nematic liquids, confined within vessels when strong anchoring at the wall produces gradients in the director field. These gradients or distortions in the director field lead to elastic stresses known as Ericksen stresses. In passing, we also note that both the flow-aligning and tumbling nematics are seen to produce large number of disclination lines under high rates of shear [53], and this observation can only be reconciled with the existence of elastic stress in the nematic medium. We will postpone this discussion to section 6, when a spatially-varying director field in the presence of flow will be considered.

4.4. Nonlinear effects

We return to the investigation of the nonlinear effects that are present in the kinetic equation. As was briefly mentioned in section 2, the nonlinear effects were manifested in the following additional terms in the kinetic (Smoluchowski) equation (26). Their effects can be analysed by considering their corrections to the symmetric and antisymmetric parts of the stress tensor separately.

4.4.1. Corrections to symmetric stress tensor. We first consider the effects of the gyroscopic term $\frac{1}{2}\alpha^2 A\partial_\beta[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w]$ on the symmetric stress tensor. Using the same method of averaging as outlined in section 4.1, we obtain

$$\begin{aligned}&\int \partial_\beta\left[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w\right]\left(u_i u_j - \frac{1}{3}\delta_{ij}\right)\mathrm{d}\boldsymbol{u}\\ &\qquad = -\int \partial_\beta\left(u_i u_j - \frac{1}{3}\delta_{ij}\right)(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w\,\mathrm{d}\boldsymbol{u}.\end{aligned}\tag{101}$$

Expanding $\boldsymbol{\Omega} = \frac{1}{2}\tilde{p}(\boldsymbol{u}\times g^s\cdot\boldsymbol{u}) + \frac{1}{2}(\boldsymbol{u}\times g^a\cdot\boldsymbol{u})$, the integral (101) can be evaluated to give the correction that is added to the symmetric stress tensor in the original equation (73):

$$\sigma^s_{ij} = -\frac{kT}{2\alpha^2}\tilde{p}\left[\frac{\partial Q_{ij}}{\partial t} - G_{ij} - M_{ij}\right]\tag{102}$$

where Q_{ij} and G_{ij} were given by (73)–(76), and we also have the nonlinear addition $\sigma^{\mathrm{NL}}_{ij} = -\frac{kT}{2\alpha^2}\tilde{p}M_{ij}$. The next step involves expanding all moments of $\boldsymbol{u}$. The tensor M_{ij}, after manipulations, takes the form

$$\begin{aligned}M_{ij} = \alpha^2\frac{A}{2}&\left[-\tilde{p}\epsilon_{\alpha\beta\gamma}g^s_{\gamma l}(\nabla\times\boldsymbol{v})_p\langle u_\alpha u_\beta u_l u_i u_j u_p\rangle\right]\\ &+\alpha^2\frac{A}{2}\left\{\frac{1}{2}\tilde{p}S_4(\boldsymbol{n}\cdot\nabla\times\boldsymbol{v})\left[n_i(\boldsymbol{n}\times g^s\cdot\boldsymbol{n})_j + n_j(\boldsymbol{n}\times g^s\cdot\boldsymbol{n})_i\right]\right.\\ &+\frac{1}{2}\tilde{p}A'\left(g^a_{im}g^s_{mj} - g^s_{im}g^a_{mj}\right)\\ &+\frac{1}{2}\tilde{p}B\big[(\nabla\times\boldsymbol{v})_i(\boldsymbol{n}\times g^s\cdot\boldsymbol{n})_j + n_i(\boldsymbol{n}\times g^s(\nabla\times\boldsymbol{v}))_j\\ &+n_i((\nabla\times\boldsymbol{v})\times g^s\cdot\boldsymbol{n})_j + (\boldsymbol{n}\cdot\nabla\times\boldsymbol{v})g^s_{mi}n_l\epsilon_{jlm} + (i\leftrightarrow j\ \text{terms})\big]\end{aligned}$$

$$
\begin{aligned}
&+\frac{1}{2}S_4(\boldsymbol{n}\cdot\nabla\times\boldsymbol{v})[n_i(\boldsymbol{n}\times g^a\cdot\boldsymbol{n})_j+n_j(\boldsymbol{n}\times g^a\cdot\boldsymbol{n})_i]\\
&+A'\left[2(\nabla\times\boldsymbol{v})_i(\nabla\times\boldsymbol{v})_j+g^a_{im}g^a_{mj}\right]\\
&+\frac{1}{2}B\left[2(\boldsymbol{n}\cdot\nabla\times\boldsymbol{v})n_i(\nabla\times\boldsymbol{v})_j+(\nabla\times\boldsymbol{v})_i(\boldsymbol{n}\times g^a\cdot\boldsymbol{n})_j\right.\\
&+n_i\left(\boldsymbol{n}\times g^a\cdot(\nabla\times\boldsymbol{v})\right)_j+n_i\left((\nabla\times\boldsymbol{v})\times g^a\cdot\boldsymbol{n}\right)_j\\
&\left.\left.+(\boldsymbol{n}\cdot\nabla\times\boldsymbol{v})g^a_{mi}n_l\epsilon_{jlm}+(i\leftrightarrow j\text{ terms})\right]\right\}.
\end{aligned}
\tag{103}
$$

Equation (103) shows that all terms are indeed second order in velocity gradient, with their coefficients expressed by the appropriate order parameters and obeying certain symmetry patterns. At this stage, we are motivated by the fact that experimentally it is not easy to measure all of the Leslie's coefficients. What is often measured is the Miesovicz viscosity defined in the beginning of section 3:

$$
\eta_a=\tfrac{1}{2}\alpha_4,\qquad \eta_b=\tfrac{1}{2}(\alpha_3+\alpha_4+\alpha_6),\qquad \eta_c=\tfrac{1}{2}(-\alpha_2+\alpha_4+\alpha_5).
\tag{104}
$$

When each flow configuration is considered, we discover that all terms in equation (103) vanish in one way or another. It seems to suggest that the effects of nonlinear corrections only manifest themselves in some non-trivial flow configurations which involve the director and flow couplings. On the other hand, some insights can be gained from consideration of the effects of nonlinearity on the antisymmetric stress tensor.

4.4.2. Corrections to antisymmetric stress tensor. The nonlinear corrections pertaining to the gyroscopic effects manifest itself strongly in the antisymmetric stress tensor, since it relates to the energy or entropy dissipation via rotation of the director axis in shear flow. The gyroscopic term changes the 'shape' of the distribution function which corresponds to energy loss via torques.

In steady state, the kinetic equation (26) becomes

$$
\begin{aligned}
\alpha\partial_\beta(\Omega_\beta w)&=\alpha^2\partial_\beta\left(\partial_\beta w-\frac{\Gamma_\beta}{kT}w\right)+\alpha^2\partial_\beta(\Omega_\alpha\partial_\alpha\Omega_\beta w)\\
&\quad+\frac{A}{2}\alpha^2\partial_\beta[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w]+\alpha\partial_\beta(\Omega_\alpha\partial_\alpha\Omega_\beta w)
\end{aligned}
\tag{105}
$$

and we write the non-equilibrium distribution function with corrections:

$$
w=w_0(1+h^{(1)}[\boldsymbol{u}]+h^{(2)}[\boldsymbol{u}])
\tag{106}
$$

where $h^{(1)}$ is the correction to the equilibrium distribution function w_0 that we had discussed before which is proportional to linear velocity gradient. $h^{(2)}[\boldsymbol{u}]$ is introduced to represent corrections that are second order in velocity gradients, and is relevant in this section since we are primarily interested in seeking nonlinear corrections to the antisymmetric stress tensor due to the gyroscopic term $\alpha^2\frac{A}{2}\partial_\beta[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w]$. As such we can, for the moment, neglect the term $\alpha\partial_\beta(\Omega_\alpha\partial_\alpha\Omega_\beta w)$, and consider only the reduced equation:

$$
\begin{aligned}
&\alpha\left(\partial^2h^{(2)}-\frac{\partial_\beta U}{kT}\partial_\beta h^{(2)}\right)-h^{(1)}\partial_k\Omega_k+\frac{\partial_k U}{kT}\Omega_k h^{(1)}-\Omega_k\partial_k h^{(1)}\\
&\qquad=\alpha\frac{A}{2}\partial_\beta[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w]
\end{aligned}
\tag{107}
$$

which we obtain after substituting (106) into (105). We have deliberately left the gyroscopic term on the right-hand side. The various terms can be evaluated explicitly in spherical coordinates, $\boldsymbol{u} = \boldsymbol{n}\cos\theta + \boldsymbol{e}\sin\theta$. The right-hand side of equation (107) yields

$$\frac{A}{2}\partial_\beta[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{\Omega}\times\boldsymbol{u})_\beta w]$$
$$= \frac{A}{2}\left\{\frac{1}{2}\tilde{p}\left[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{n}\times\boldsymbol{e})\cdot g^s\cdot\boldsymbol{u}\frac{1}{kT}\frac{\partial U}{\partial\theta} - (g^a\cdot\boldsymbol{u})(g^s\cdot\boldsymbol{u})\right]\right.$$
$$\left. + \frac{1}{2}\left[(\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})(\boldsymbol{n}\times\boldsymbol{e})\cdot g^a\cdot\boldsymbol{u}\frac{1}{kT}\frac{\partial U}{\partial\theta} - (g^a\cdot\boldsymbol{u})^2\right] - (\boldsymbol{u}\cdot\nabla\times\boldsymbol{v})^2\right\}. \tag{108}$$

We seek the appropriate general expression of $h^{(2)}$ that corresponds to equation (108). The corrections due to $h^{(1)}$ becomes irrelevant since no matching of the velocity gradient terms can be found. An appropriate expression for $h^{(2)}$ will be $h^{(2)} = h_1 + h_2 + h_3$ where

$$\begin{aligned} h_1 = {} & h_{p1}g^s_{\alpha\beta}g^a_{ij}\epsilon_{\gamma ij}(\boldsymbol{n}\times\boldsymbol{e})_\alpha n_\gamma n_\beta + h_{p2}g^s_{\alpha\beta}g^a_{ij}\epsilon_{\gamma ij}(\boldsymbol{n}\times\boldsymbol{e})_\alpha n_\gamma e_\beta \\ & + h_{p3}g^s_{\alpha\beta}g^a_{ij}\epsilon_{\gamma ij}(\boldsymbol{n}\times\boldsymbol{e})_\alpha e_\gamma e_\beta + h_{p4}g^s_{\alpha\beta}g^a_{ij}\epsilon_{\gamma ij}(\boldsymbol{n}\times\boldsymbol{e})_\alpha e_\gamma n_\beta \\ & + h_{p5}g^s_{m\alpha}g^a_{m\beta}n_\alpha n_\beta + h_{p6}g^s_{m\alpha}g^a_{m\beta}e_\alpha e_\beta + h_{p7}g^s_{m\alpha}g^a_{m\beta}n_\alpha e_\beta \\ & + h_{p8}g^s_{m\alpha}g^a_{m\beta}e_\alpha n_\beta \end{aligned} \tag{109}$$

where the correction coefficients must depend on the two angles $h = h(\theta,\phi)$.

The term h_2 has exactly the same general expansions as h_1 above, except for every symmetric velocity gradient $g^s_{\alpha\beta}$ in these equations, we replace it by $g^a_{\alpha\beta}$. Finally we have for h_3:

$$\begin{aligned} h_3 = {} & h_a\epsilon_{\alpha jk}\epsilon_{\beta mn}g^a_{jk}g^a_{mn}n_\alpha n_\beta + h_b\epsilon_{\alpha jk}\epsilon_{\beta mn}g^a_{jk}g^a_{mn}e_\alpha e_\beta \\ & + h_c\epsilon_{\alpha jk}\epsilon_{\beta mn}g^a_{jk}g^a_{mn}n_\alpha e_\beta + h_d\epsilon_{\alpha jk}\epsilon_{\beta mn}g^a_{jk}g^a_{mn}e_\alpha n_\beta. \end{aligned} \tag{110}$$

The left-hand side of equation (107) can be evaluated explicitly in spherical polar coordinates to give

$$\frac{\partial^2 h^{(2)}}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h^{(2)}}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 h^{(2)}}{\partial\phi^2}. \tag{111}$$

Substituting h_1, h_2 and h_3 into equation (111), and after a series of tedious algebra, we arrive at a form where explicit comparison on both sides can be made. For coefficients corresponding to h_1, we obtain the following relations:

$$\frac{\partial^2 h_{p1}}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_{p1}}{\partial\theta} - \frac{h_{p1}}{\sin^2\theta} = \frac{A}{8}\tilde{p}\cos^2\theta\frac{1}{kT}\frac{\partial U}{\partial\theta} \tag{112}$$

$$\frac{\partial^2 h_{p2}}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_{p2}}{\partial\theta} - \frac{2h_{p2}}{\sin^2\theta} = \frac{A}{8}\tilde{p}\cos\theta\sin\theta\frac{1}{kT}\frac{\partial U}{\partial\theta} \tag{113}$$

$$\frac{\partial^2 h_{p3}}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_{p3}}{\partial\theta} - \frac{3h_{p3}}{\sin^2\theta} = \frac{A}{8}\tilde{p}\sin^2\theta\frac{1}{kT}\frac{\partial U}{\partial\theta} \tag{114}$$

$$\frac{\partial^2 h_{p5}}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_{p5}}{\partial\theta} - \frac{2h_{p6}}{\sin^2\theta} = -\frac{A}{4}\tilde{p}\cos^2\theta \tag{115}$$

$$\frac{\partial^2 h_{p6}}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_{p6}}{\partial\theta} - \frac{4h_{p6}}{\sin^2\theta} = -\frac{A}{4}\tilde{p}\sin^2\theta \tag{116}$$

$$\frac{\partial^2 h_{p7}}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_{p7}}{\partial\theta} - \frac{h_{p7}}{\sin^2\theta} = -\frac{A}{4}\tilde{p}\cos\theta\sin\theta. \tag{117}$$

For coefficients corresponding to h_2, we arrive at the same equations as h_1 but without the form factor $\tilde{p}$. For coefficients corresponding to h_3,

$$\frac{\partial^2 h_a}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_a}{\partial\theta} = -\frac{A}{8}\cos^2\theta \tag{118}$$

$$\frac{\partial^2 h_b}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_b}{\partial\theta} - 2\frac{h_b}{\sin^2\theta} = -\frac{A}{8}\sin^2\theta \tag{119}$$

$$\frac{\partial^2 h_c}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U}{\partial\theta}\right)\frac{\partial h_c}{\partial\theta} - \frac{h_c}{\sin^2\theta} = -\frac{A}{8}\sin\theta\cos\theta \tag{120}$$

and $h_d = h_c$, $h_{p4} = h_{p2}$, $h_{p8} = h_{p7}$.

We wish to obtain some qualitative features of the modified stress tensor due to the nonlinear gyroscopic term; therefore, we make the following approximations.

(1) We use the one-constant approximation, that is, we assume that all the h for a given combination of velocity gradients are equal, $h_{p1} = h_{p2} = h_{p3} = h_{p4}$, $h_{p5} = h_{p6} = h_{p7} = h_{p8}$, and $h_a = h_b = h_c = h_d = h'_3$, so that

$$\begin{aligned} h^{(2)} = {} & h_{p1} g^s_{\alpha\beta} g^a_{ij} \epsilon_{\gamma ij} (\boldsymbol{n}\times\boldsymbol{e})_\alpha [n_\gamma n_\beta + n_\gamma e_\beta + e_\gamma e_\beta + e_\gamma n_\beta] \\ & + h_{p5} g^s_{m\alpha} g^a_{m\beta} [n_\alpha n_\beta + e_\alpha e_\beta + n_\alpha e_\beta + e_\alpha n_\beta] \\ & + h_{a1} g^a_{\alpha\beta} g^a_{ij} \epsilon_{\gamma ij} (\boldsymbol{n}\times\boldsymbol{e})_\alpha [n_\gamma n_\beta + n_\gamma e_\beta + e_\gamma e_\beta + e_\gamma n_\beta] \\ & + h_{a5} g^a_{m\alpha} g^a_{m\beta} [n_\alpha n_\beta + e_\alpha e_\beta + n_\alpha e_\beta + e_\alpha n_\beta] \\ & + h'_3 \epsilon_{\alpha jk} \epsilon_{\beta mn} g^a_{jk} g^a_{mn} [n_\alpha n_\beta + e_\alpha e_\beta + n_\alpha e_\beta + e_\alpha n_\beta] \end{aligned} \tag{121}$$

where h_{a1} and h_{a5} are terms due to h_2.

(2) We assume that in all cases, the term $h_p/\sin^2\theta$ will be negligible if the relaxation time of the molecular rotation about the director $\boldsymbol{n}$ is much smaller than the time of reorientation with respect to the angle θ. In this way, the microscopic antisymmetric stress tensor due to gyroscopic effects can be calculated using the formula

$$\sigma^a_{\alpha\beta} = \int w\sigma^{\text{micro}}_{\alpha\beta}\,\mathrm{d}\boldsymbol{u} = \int w_0 h \sigma^{\text{micro}}_{\alpha\beta}\,\mathrm{d}\boldsymbol{u}. \tag{122}$$

Substituting equation (121) and carry out the calculation explicitly, we eventually arrive at (after restoring dimensional variables):

$$\begin{aligned} \sigma^a_{\alpha\beta} = \int \Bigg(& -\rho\lambda_\perp (\boldsymbol{n}\cdot\nabla\times\boldsymbol{v})[n_\alpha(\boldsymbol{n}\times g^s\cdot\boldsymbol{n})_\beta - n_\beta(\boldsymbol{n}\times g^s\cdot\boldsymbol{n})_\alpha]\cdot h_{p1} \\ & - \frac{\rho\lambda_\perp}{2}\left\{ n_\alpha[g^a\cdot g^s\cdot\boldsymbol{n}]_\beta + n_\alpha[g^s\cdot g^s\cdot\boldsymbol{n}]_\beta + n_\beta[g^a\cdot g^s\cdot\boldsymbol{n}]_\alpha + n_\beta[g^s\cdot g^s\cdot\boldsymbol{n}]_\alpha \right\}\cdot h_{p5} \\ & + 4\rho\lambda_\perp(\boldsymbol{n}\cdot\nabla\times\boldsymbol{v})[n_\alpha(\nabla\times\boldsymbol{v})_\beta - n_\beta(\nabla\times\boldsymbol{v})_\alpha]\cdot h'_3 \Bigg)\frac{\partial U}{\partial\theta} w_0 \sin\theta\,\mathrm{d}\theta. \end{aligned} \tag{123}$$

The coefficients h_{p1}, h_{p5} and h'_3 are derived to take the values:

$$h_{p1} \sim \frac{A}{8}\tilde{p}\frac{\pi}{q}\,\mathrm{e}^q, \qquad h_{p5} \sim -\frac{A}{4}\tilde{p}q^{-3/2}\,\mathrm{e}^q, \qquad h_2 \sim -\frac{A}{8}q^{-3/2}\,\mathrm{e}^q. \tag{124}$$

It can be seen that all terms without the potential derivatives on the right-hand side, i.e. equations (115)–(120), retain the same functional dependence of q. The exponential dependence on q, however, exists for all coefficients of h. The nonlinear rotational viscosity γ'_{p1} due to h_{p1} is found to be

$$\gamma'_{p1} = \int h_{p1}\frac{\partial U}{\partial\theta} w_0 \sin\theta\,\mathrm{d}\theta \simeq \frac{1}{16}\rho\lambda_\perp \mathrm{e}^{2q} q^{-\frac{1}{2}} A\tilde{p} \tag{125}$$

which only appears in discotic nematics with non-vanishing $A = \sqrt{I_\parallel/I_\perp}$.

4.5. Preliminary discussion points

Despite the crude assumptions made in the previous section, we managed to obtain some qualitative features of the solutions for kinetic coefficients and constitutive relations.

Equation (123) suggests that at a higher flow rate, there is strong coupling of the director with the flow vorticity. Such effects become irrelevant for a rod-like nematic when A is very small. On the other hand due to the non-vanishing $I_{\parallel}$ and hence the additional gyroscopic effects in disc-like molecules, there is a nonlinear correction to the antisymmetric stress tensor and the rotational viscosity γ_1.

The more general approach to find the complete solution to the nonlinear viscosity is to write down the full general expression for h which satisfies all symmetries of the problem, and explicit matchings of the coefficients can be made and determined. This process is however very laborious which does not necessarily yield new physical insights to the solution. Instead we had adopted a more pragmatic approach by focusing on only a subgroup of the complete expression (see equation (121)) using the one-constant approximation.

The conventional intuitive picture to explain the nonlinear effects in viscosity is to visualize flow alignment of the molecules along the flow. This microscopic rearrangement of the molecules that results in a decrease of viscosity at higher velocity gradient is commonly known as *shear-thinning mechanism*. Most suspensions of non-spherical particles which are dilute enough tend to be shear-thinning at modest rates of shear. No doubt flow alignment is always partly responsible but there is an additional factor due to rotation of suspended particles by planar shear to adopt a layered arrangement which favours easy shear. In some cases, at even higher rates of shear, the layers may break up due to *shear-thickening*, when the particles form a less regular structure such that they occupy a larger volume and the bulk structure becomes stiffer. The removal of misaligned domains therefore results in a drop in the viscosity. Strain rate then speeds up and eventually a steady state is achieved at an alignment angle (monodomain). However above a critical shear rate there is no solution for the steady-state angle of alignment and this results in instabilities such as the tumbling phenomena discussed before.

As was briefly mentioned above, we can derive γ_1 in the linear regime (due to $h^{(1)}$ correction) using the method described in this section. This method predicts an exponential dependence on q, where q represents mean-field coupling strength which is proportional to the order parameter S_2. The apparent contradiction with the result of (93) can be resolved if one expands the denominator in the limit of small q.

5. Rotational friction constant

In this section, the rotational friction constant $\lambda_{\perp}$ is discussed in greater detail. We show how it can be derived from microscopic interactions for a discotic nematic liquid crystal. The expression for this constant suggests an Arrhenius exponential dependence on the isotropic part of the intermolecular potential.

5.1. Generalized fluctuation–dissipation theorem

So far we have studied Brownian motion as a physical realization of a random process. For our model of a molecule in rotational motion, the nature of the medium entered our consideration only through one parameter, the friction constant. We know, however, that that the medium comprises other molecules that are ultimately subjected to deterministic, not statistical evolution. Therefore we ought to be able to derive the friction constant from basic atomic dynamics. The appropriate formalism requires us to work within the framework of generalized fluctuation–dissipation theorem. To begin with, we consider the generalized Langevin equation, also known as the Mori equation [36] that relates the friction coefficient to a memory function $K(t)$ (in the absence of external forces),

$$\frac{\mathrm{d}\boldsymbol{A}}{\mathrm{d}t} = \int_o^t K(s)\boldsymbol{A}(t-s)\,\mathrm{d}s + \boldsymbol{F}(t) \tag{126}$$

where $\boldsymbol{A}(t)$ is the dynamical variable of the problem, and $\boldsymbol{F}(t)$ is the stochastic source. The memory function $K(t)$ is related to the correlation function of the stochastic force:

$$K(t) = \frac{\langle \boldsymbol{F}(t)\boldsymbol{F}(0)\rangle}{MkT} \tag{127}$$

where M is the mass of the Brownian particle.

Equation (126) is useful when there is a good separation of time-scales for the motions of the components of the system. We note that compared to the Langevin equation, the friction constant λ has become a friction kernel, $K(t)$, which if decays to zero sufficiently rapidly, leads to

$$\int_o^t K(s)\boldsymbol{A}(t-s)\,\mathrm{d}s \approx \boldsymbol{A}(t)\int_0^t K(s)\,\mathrm{d}s \approx \boldsymbol{A}(t)\int_0^\infty K(s)\,\mathrm{d}s. \tag{128}$$

Thus the friction term in the Mori equation can be approximated by the friction term in the Langevin equation, provided that the correlation time of the random force is short compared to the time in which $\boldsymbol{A}(t)$ changes appreciably. We thus have a molecular expression for the friction constant λ, which is the time integral of the autocorrelation function of the intermolecular force exerted by the bath particles on the Brownian particle:

$$\lambda = \frac{1}{MkT}\int_0^\infty \langle \boldsymbol{F}(t)\boldsymbol{F}(0)\rangle\,\mathrm{d}t. \tag{129}$$

Here the random force is interpreted as the intermolecular force on the Brownian particle exerted by the bath particles when they move in the field of the fixed Brownian particle (note that there is nothing intrinsically random in the random force). Equation (127) states that, if we consider the Langevin's limit, when the correlation time of the stochastic force is so short as to approximate it as a δ-function,

$$\langle \boldsymbol{F}(t)\boldsymbol{F}(0)\rangle = \Xi\delta(t) \tag{130}$$

where Ξ is the stochastic strength. Substituting it to the Mori equation, we recover the fluctuation–dissipation theorem $\Xi = \lambda MkT$ (the parameter M can be rescaled to 1 depending on the definition of friction constant).

In the context of rotational motion, the friction constant arises as a consequence of the Brownian particle experiencing a field of random external torques. These instantaneous torques arise from fluctuations in the random intermolecular forces surrounding the particle. As a result, the particle executes random rotational motion with arbitrary angular velocity at any time-step. We can write down a similar form for the rotational friction constant $\lambda_\perp$:

$$\lambda_\perp \approx \frac{1}{kT}\int_0^\infty \langle \boldsymbol{\xi}(t)\boldsymbol{\xi}(0)\rangle\,\mathrm{d}t \tag{131}$$

where $\boldsymbol{\xi}(t)$ is the stochastic torque at time t.

For a dense system like a nematic liquid, we have to consider two distinct types of averaging processes in equation (131). The first type concerns *ensemble-averaging* which is performed with respect to particle distribution and takes into account short-range correlation effects etc. The second type is the *time-averaging*, where temporal correlations of the stochastic torques are considered. In this section, we will consider these two processes separately to arrive at a microscopic expression for $\lambda_\perp$.

The above analysis assumes that the decay rate of the torque correlation function is rapid with respect to the rate of change of the distribution function of the Brownian particle (see equation (128)). It can be shown that the correlation time for the stochastic torques is the effective collision time t_c which is of the same order of magnitude as the relaxation time for the angular velocity. This however is true only in the stretched limit of the Brownian particle being truly small (e.g. molecular liquids). For massive molecules, one expects the correlation time to be much longer than the collision time (often neglected in this case) and the correlation time is equated to the *Brownian motion time* t_w. Strictly speaking that this only holds true when $t_c \ll t \ll t_w$. There is an observation of long time-tail in molecular correlation functions [36, 54] i.e. decay of certain molecular correlation function has an asymptotic slow inverse power law; not the rapid exponential decay that had been assumed. Hence the assumption that K has a short lifetime relative to A may not strictly be true. This can be explained via the existence of slow fluid variables, and the general theoretical framework is known as mode–mode coupling theory. We shall, however, not deal with this aspect since it is beyond the scope of this review.

An example is that of a dilute gas as first suggested by Kirkwood [1]. Here two widely different time-scales are easily identified as the duration of a collision and the mean free flight time. The collision time may be interpreted as the time in which the motion of a molecule is predictable from a knowledge of its initial momentum and the force on it at the initial instant. For times longer than this collision time, a second collision may occur, completely uncorrelated with the first. The mean-free time describes this regime well and it may be interpreted as the decay time of the particle's momentum correlation function.

5.2. Time averaging

As mentioned before, the temporal averaging of the stochastic torques $\langle \boldsymbol{\xi}(t)\boldsymbol{\xi}(0)\rangle$ corresponds to finding the autocorrelation function of the angular velocity [1]. Such correlation function typically follows an exponentially decaying function, where the decay time is often called the Brownian motion time since it is the time above which the motion becomes diffusive, and below which the motion is ballistic. By finding this correlation time for the particle's angular momentum, one effectively finds the correlation time for the stochastic torques. However, for a nematic executing rotational motion, the situation is complicated by the presence of multiple-correlation times due to its non-trivial tensorial formalism and the anisotropy of the molecules. This contrasts with a typical isotropic liquid where the molecular relaxation process can usually be described in terms of a single correlation time τ_c.

Some insights on the Brownian motion time can be drawn from the translational motion of a Brownian particle of mass M, such as in the case of a colloid particle. In this case we consider the dynamical variable velocity $\boldsymbol{v}(t)$, whose correlation function obeys

$$\langle \boldsymbol{v}(t)\boldsymbol{v}(t')\rangle = \frac{kT}{M}\,\mathrm{e}^{-|t-t'|/\tau}, \tag{132}$$

where $\tau = M/\lambda_t$ is the Brownian motion time, or the velocity correlation time. λ_t denotes the translational friction constant. Analogously, we can define a similar correlation time τ_ω for the angular velocity $\boldsymbol{\omega}$ for rotational motion. For $t < \tau_\omega$, the rotational motion is 'ballistic' in the sense that the angular velocity is maintained without 'collisions', which come in the form of contacts with random external torques acting on the system. For $t > \tau_w$, the rotational motion becomes diffusive and the particle distribution function eventually reaches the equilibrium Maxwell velocity distribution $\mathrm{e}^{-I\omega^2/2kT}$, hence the name rotational Brownian motion time [36]. For a simple spherical molecule, the dynamics can be described with a single Brownian motion time $\tau_r = I/\lambda_r$, where λ_r is now the rotational friction constant and I is the moment of inertia (analogous to the mass in translational motion).

The Brownian motion time for non-spherical molecules are however complicated by both the rotations around the long molecular axis and the large-angle rotations around the shorter molecular axis. It is clear that the larger the moment of inertia the longer the particle maintains its correlation in angular velocity before it enters the diffusive regime. The cross-over from Brownian to non-Brownian behaviour in a flowing suspension is controlled by the *rotational Peclet number* $Pe = \dot{\gamma}/D_r$ where D_r is the rotary diffusivity of the particles and $\dot{\gamma}$ is the strain rate.

The rotational Brownian motion time is not to be confused with another relaxation time τ_u which is the time it takes to relax slowly to the Boltzmann distribution over the angular coordinates, given by $\exp[-U(\mathbf{n}\cdot\mathbf{u})/kT]$ where $U(\mathbf{n}\cdot\mathbf{u})$ is the mean-field potential experienced by the molecule. The characteristic time-scale τ_u is approximately $\sqrt{I_\perp/kT}$ if we assume rotational motions to be dominated by large-angle rotations about the short molecular axis. This is the regime where our kinetic equation is based upon and leads to the mode relaxation times evaluated in section 2.

It might be tempting to think that the solution for a disc-like molecule in rotational Brownian motion will yield only a trivial modification to the correlation time of a long rod (where the relaxation times for rotations around the long molecular axis is very small and can be neglected). In fact, as we shall see, due to both rotations along and perpendicular to the molecular axis in discotic nematics, non-trivial solutions for the Brownian motion time can be found.

For a discotic nematic phase, due to the significant moment of inertia parallel to the director axis $I_\parallel$, the axial angular momentum $I_\parallel\dot{\phi}$ along the molecular axis may be comparable to or larger than that perpendicular to the axis. From our analysis of the kinetic equation (11) before, we have the following equation:

$$I_\perp\dot{\omega}_\alpha = -\lambda_\perp\omega_\alpha + \xi_\alpha - I_\parallel\dot{\psi}(\boldsymbol{\omega}\times\boldsymbol{u})_\alpha \tag{133}$$

where for simplicity we have assumed zero external torque and external flow. $I_\parallel\dot{\psi}$ can be assumed to be almost constant since there is virtually no torque acting on the axis and hence no angular acceleration along the director. Clearly the description for rotational motion is more complicated due to its vectorial form and the precessional term $I_\parallel\dot{\psi}(\boldsymbol{\omega}\times\boldsymbol{u})$, giving non-trivial solutions as $I_\parallel/I_\perp$ is non-negligible. Expanding the cross product in tensorial form, equation (133) becomes

$$\dot{\omega}_\alpha = -\lambda_{\alpha\beta}\omega_\beta + \frac{\xi_\alpha}{I_\perp} \tag{134}$$

where

$$\lambda_{\alpha\beta} = \frac{\lambda_\perp}{I_\perp}\delta_{\alpha\beta} + A^2\dot{\psi}\epsilon_{\alpha\beta\gamma}u_\gamma \qquad \text{with} \qquad A = \sqrt{I_\parallel/I_\perp}. \tag{135}$$

The problem is similar to solving small oscillation dynamics using normal mode expansion. The general motion is then a superposition of the various normal modes with the mode frequencies and their amplitudes given by the eigenvalues and eigenvectors of the matrix respectively. Setting the equation in homogeneous form ($\xi_\alpha/I_\perp = 0$) and assuming that the director coordinate u_γ remains approximately stationary on the fast time-scale of $\boldsymbol{\omega}$, we have, writing $K_\gamma = A^2\dot{\psi}u_\gamma$,

$$\begin{pmatrix}\dot{\omega}_1\\ \dot{\omega}_2\\ \dot{\omega}_3\end{pmatrix} = \begin{pmatrix}-\lambda_\perp/I_\perp & -K_3 & K_2\\ K_3 & -\lambda_\perp/I_\perp & -K_1\\ -K_2 & K_1 & -\lambda_\perp/I_\perp\end{pmatrix}\begin{pmatrix}\omega_1\\ \omega_2\\ \omega_3\end{pmatrix}. \tag{136}$$

Here we note that the matrix is non-symmetric, and complex eigenvalues are to be expected. Direct diagonalization of the matrix numerically gives the following eigenvalues and eigenvectors:

$$\lambda_1 = -\frac{\lambda_\perp}{I_\perp}, \qquad \lambda_{2,3} = -\frac{\lambda_\perp}{I_\perp} \pm \mathrm{i}A^2\dot{\psi} \tag{137}$$

and the eigenvectors are

$$\boldsymbol{v}_1 = \begin{pmatrix} 1 \\ K_2/K_1 \\ K_3/K_1 \end{pmatrix}, \qquad \boldsymbol{v}_{2,3} = \begin{pmatrix} (\pm\mathrm{i}A^2\dot{\psi}K_3 - K_1K_2)/\left(K_1^2 + K_3^2\right) \\ 1 \\ (\mp\mathrm{i}A^2\dot{\psi}K_1 - K_2K_3)/\left(K_1^2 + K_3^2\right) \end{pmatrix}. \tag{138}$$

It is clear that the eigenvalues become degenerate $\lambda_1 = \lambda_2 = \lambda_3 = -\lambda_\perp/I_\perp$ for the case of rod-like molecules, indicating the presence of a single Brownian motion time corresponding to only rotations of the long molecular axis.

The angular velocity components can be written as

$$\begin{aligned} \omega_1 &= \mathrm{e}^{-t/\tau}\left[1 - 2\frac{K_1K_2}{K_1^2 + K_3^2}\cos(A^2\dot{\psi}t) - 2\frac{K_3A^2\dot{\psi}}{K_1^2 + K_3^2}\sin(A^2\dot{\psi}t)\right] \\ \omega_2 &= \mathrm{e}^{-t/\tau}\left[\frac{K_2}{K_1} + 2\cos(A^2\dot{\psi}t)\right] \\ \omega_3 &= \mathrm{e}^{-t/\tau}\left[\frac{K_3}{K_1} - 2\frac{K_2K_3}{K_1^2 + K_3^2}\cos(A^2\dot{\psi}t) + 2\frac{K_1A^2\dot{\psi}}{K_1^2 + K_3^2}\sin(A^2\dot{\psi}t)\right] \end{aligned} \tag{139}$$

where we have defined $\tau = I_\perp/\lambda_\perp$ as the rotational Brownian motion time.

The stochastic force ξ_α introduces inhomogeneity into the equation and the full solution of the inhomogeneous equation can be obtained by integrating over the stochastic term in equation (134). For simplicity we consider just one of the angular velocity components ω_2 and its correlation function $\langle\omega_2(t)\omega_2(0)\rangle$. Careful analysis leads to the following expression for the angular velocity correlation function:

$$\begin{aligned} \langle\omega_2(t)\omega_2(0)\rangle = {}& \frac{kT}{I_\perp}\left(\frac{K_2}{K_1}\right)^2 \mathrm{e}^{-t/\tau} + \frac{kT}{I_\perp}\mathrm{e}^{-t/\tau}\cos(t/\tau_\psi) \\ & + \frac{kT}{I_\perp}\left(\frac{K_2}{K_1}\right)\mathrm{e}^{-t/\tau}\left[\frac{\tau\tau_\psi}{\tau_\psi^2 + \tau^2}\right]\left[2\frac{\tau_\psi}{\tau}\cos(t/\tau_\psi) - \sin(t/\tau_\psi)\right] \\ & + \frac{kT}{I_\perp}\mathrm{e}^{-t/\tau}\left[\frac{\tau\tau_\psi}{\tau_\psi^2 + \tau^2}\right]\left[\frac{\tau_\psi}{\tau}\cos(t/\tau_\psi) - \sin(t/\tau_\psi)\right]. \end{aligned} \tag{140}$$

The first term gives the natural decay of the correlation function for the angular velocity which depends on the geometrical projection ratio K_2/K_1. The imaginary part of the eigenvalues gives rise to the precessional term $\cos(t/\tau_\psi)$ where the precessional period $\tau_\psi = 1/A^2\dot{\psi}$ is introduced. Explicit comparison between the two time-scales can be made:

$$\frac{\tau}{\tau_\psi} = \frac{kTI_\perp}{\lambda_\perp^2}\frac{I_\parallel}{I_\perp} \tag{141}$$

The first term on the right-hand side corresponds to the small parameter α we had defined in equation (16); therefore, we conclude that τ is significantly smaller than τ_ψ for disc-like molecules. Rearranging the terms we have for $t < \tau \ll \tau_\psi$,

$$\langle\omega_2(t)\omega_2(0)\rangle = \frac{kT}{I_\perp}\mathrm{e}^{-t/\tau}\left[\left(\frac{K_2}{K_1}\right)^2 + 2\frac{K_2}{K_1}\left(1 + \frac{K_2}{K_1}\right)\right]. \tag{142}$$

Note that except for the prefactor in terms of K's, equation (142) resembles (132) in translational motion. We conclude that the system remains heavily damped, and the effective correlation or relaxation time is the shorter time-scale τ. This corresponds to the assumption that thermalization occurs on a time-scale much shorter with respect to the time for appreciable changes in positional distances. This occurs when the rotational friction constant $\lambda_\perp$ is large and is often called the high friction limit. Note that the rotational Brownian motion time has a linear dependence on the friction constant $\lambda_\perp$ which is to be contrasted with the mode relaxation time found in section 2 which has an inverse dependence on $\lambda_\perp$.

Equation (131) therefore becomes

$$\lambda_\perp \approx \frac{1}{kT}\int_0^\infty \langle \xi^2(0)\rangle_{\mathrm{ens}}\, \mathrm{e}^{-t/\tau_w}\, \mathrm{d}t \tag{143}$$

giving the final form of friction constant after time-averaging:

$$\lambda_\perp \approx \sqrt{\frac{I_\perp}{kT}}\sqrt{\langle \xi^2(0)\rangle_{\mathrm{ens}}} \tag{144}$$

where $\langle \xi^2\rangle_{\mathrm{ens}}$ denotes ensemble averaging of the stochastic torques acting on the molecules.

5.3. Ensemble averaging

As mentioned before, the idea of ensemble averaging is essential when considering macroscopic properties of any dense liquid. The ensemble averaging of the torques in equation (143) describes microscopically the interactions of the molecules with various random potentials exerted by the surrounding molecules. A reasonable expression for $\langle \xi^2(0)\rangle_{ens}$ for molecule 1 can be written as

$$\langle \xi^2\rangle_{\mathrm{ens}} \simeq N^2 \int \partial_1 U(1,2)\cdot \partial_1 U(1,3) W_3(1,2,3) d(1)d(2)d(3) \tag{145}$$

where $\partial_{1k} = \epsilon_{kij} u_{1i}\partial/\partial u_{1j}$, $d(1) = \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{u}_1$ and $W_3(1,2,3)$ is the three-particle angular distribution function. $\partial_1 U(1,2)$ describes the torque exerted by molecule 2 on molecule 1 due to their pair interaction potential $U(1,2)$, and the same holds for $\partial_1 U(1,3)$.

To evaluate this ensemble we need to have a microscopic model of the molecular pair potential that acts on a particular pair of nematic molecules. We begin this by giving a brief review of the mean-field description of the intermolecular forces, followed by an attempt to build a phenomenological model that goes beyond mean-field regime and consider more realistic effects such as short-range orientational correlations and the excluded volume effects, paying specific attention to the case of a discotic nematic.

5.3.1. Nematic intermolecular forces. The molecular theory of the nematics has been an intense field of research in the past decades, using advanced statistical approaches such as the density functional theory. Two main lines were pursued to derive the various thermodynamic quantities that agree with the experimental results.

1. Treating the intermolecular attraction forces as anisotropic and the intermolecular repulsions as isotropic to first approximation, which serves as a positive pressure. The result is temperature-dependent of course.
2. In suspensions of anisotropic particles the nematic order arises purely from short-range anisotropic repulsive forces (exclusion volume effects in the Onsager approach). The high density of the liquid is established by the intermolecular attractions, which are assumed to be isotropic.

Here we demonstrate a combined approach that takes into account both anisotropic intermolecular attractive forces depending on the orientation of the interacting molecules, but at the same time considers the anisotropic repulsive potential which arises from the exclusion volume effects. We consider the following expression for the effective uniaxial potential [55]

$$V_{\rm eff}(\boldsymbol{u}_i, \boldsymbol{r}_{ij}, \boldsymbol{u}_j) = V_{\rm iso} - J_1(\boldsymbol{r})(\boldsymbol{u}_i \cdot \boldsymbol{u}_j)^2 - J_2(\boldsymbol{r})[(\boldsymbol{u}_i \cdot \boldsymbol{r}_{ij})^2 + (\boldsymbol{u}_j \cdot \boldsymbol{r}_{ij})^2] \\ - J_3(\boldsymbol{r})[(\boldsymbol{u}_i \cdot \boldsymbol{u}_j)(\boldsymbol{u}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{u}_j \cdot \boldsymbol{r}_{ij})] \quad (146)$$

where $V_{\rm iso}$ represents an isotropic dispersion potential independent of $\boldsymbol{u}$'s and the various J's represent the orientation-dependent coupling strengths which can be expressed in terms of the electric dipole and quadrupole matrix elements. $\boldsymbol{u}$ denotes the molecular director while $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ denotes the molecular distance from particle i to j. See figure 4 for the geometric illustration. Chandrasekhar *et al* [56] had argued that the potential arises mainly from the dispersion forces which have r^{-6} or $r^{-8/3}$ dependence on the intermolecular separation for dipole–dipole and dipole–quadrupole interactions, respectively. The permanent dipoles are found to play a minor role in providing the stability of the nematic phase (although dipole–dipole forces are much stronger than the van der Waals, in practice, dipolar molecules in liquid always form very strong dimers).

As shown by Baron and Gelbart [57], the predominant orientational interaction in nematics must be the isotropic dispersion attraction modulated by the anisotropic molecular hard core. The isotropic part of the dispersion interaction is generally greater than the anisotropic part because it is proportional to the average molecular polarizability. The anisotropy of this overall potential comes mainly from the asymmetric molecular shape. Thus this effective potential is a combination of intermolecular attraction and repulsion,

$$V_{\rm eff}(1, 2) = J_{\rm att}(r_{12})\Theta(r_{12} - \xi_{12}) \quad (147)$$

where the step function $\Theta(r_{12} - \xi_{12})$ determines the steric cut-off.

5.3.2. Mean-field theory: the Maier–Saupe potential. The simplest molecular theory of the nematics can be developed in the context of a mean-field approximation. By mean-field approximation we mean that all correlations between different molecules, such as the fluctuations in the short-range order (mutual alignment of two neighbouring molecules), are ignored. This is obviously a crude approximation but it does enable one to obtain very simple and useful expressions for the free energy.

In this section, we demonstrate how the mean-field approximation can be established starting with a completely general pairwise intermolecular interaction potential. One appropriate model potential is to write it as an expansion in terms of Legendre polynomials (spherical invariants) P_{lm} [55], depending only on the unit vectors $\boldsymbol{u}_1 = \boldsymbol{r}_1/|\boldsymbol{r}_1|, \boldsymbol{u}_{12} = \boldsymbol{r}_{12}/|\boldsymbol{r}_{12}|$, etc:

$$U(\boldsymbol{u}_1, \boldsymbol{u}_{12}, \boldsymbol{u}_2) = \sum_{l,m} J_{lm}(\boldsymbol{u}_{12}) P_{lm}(\boldsymbol{u}_1, \boldsymbol{u}_{12}, \boldsymbol{u}_2). \quad (148)$$

To obtain the single molecule potential U in the mean-field approximation it is necessary to take successive averages of the intermolecular potential U_{12}. Firstly we note that in the nematic phase there is no positional order and the molecular centres are distributed randomly. If one neglects the positional correlations, the interaction potential can be further simplified by averaging over all values of the intermolecular unit vector $\boldsymbol{u}_{12}$:

$$\tilde{U}(\boldsymbol{u}_1, \boldsymbol{u}_2) = \int U(\boldsymbol{u}_1, \boldsymbol{u}_{12}, \boldsymbol{u}_2)\, {\rm d}\boldsymbol{u}_{12}. \quad (149)$$

The final mean-field potential $U_{MF}(\boldsymbol{u}_1)$ is obtained by averaging over all orientations of the second molecule $\boldsymbol{u}_2$:

$$U_{MF}(\boldsymbol{u}_1) = \int \tilde{U}(\boldsymbol{u}_1, \boldsymbol{u}_2) w_1(\boldsymbol{u}_2)\, \mathrm{d}\boldsymbol{u}_2 \tag{150}$$

where $\boldsymbol{u}_i$ specifies the orientation of the molecule i, and

$$w_1(\boldsymbol{u}_i) = \frac{1}{Z}\, \mathrm{e}^{-\beta U_{MF}(\boldsymbol{u}_i)} \tag{151}$$

denotes the single-particle distribution function that depends only on the molecular orientation. Equation (151) says that in the mean-field approximation, that is, neglecting pair correlations between $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ in (150), each molecule feels some average angular potential produced by all other molecules in the system. The usual Maier–Saupe potential $J P_2(\boldsymbol{n} \cdot \boldsymbol{u}_i)$ is obtained via this averaging process with respect to the first non-polar term in the Legendre polynomial expansion of the intermolecular potential.

5.4. Model potential for discotic nematics

Realistic intermolecular interaction potentials for mesogenic molecules can be very complex and are generally unknown. At the same time molecular theories based on simple model potentials usually offer good qualitative solutions when describing some general properties of liquid crystals that are not sensitive to the details on the interaction. In this section, we propose a simple nematic potential to model molecular interactions in a discotic nematic liquid crystal within the mean-field approximation. This leads to an explicit expression of the torque autocorrelation function in equation (145).

1. *Model pair potential*: previous investigations on the intermolecular interaction potential of a discotic nematic had focused mainly on the regime close to nematic–isotropic (N–I) transition [58]. A reasonable assumption is that the nematic order arises primarily from the short-range and highly anisotropic repulsive forces between the molecules. We consider a modification of the nematic potential in equation (146) which captures the essential physics of the molecular interactions in a discotic nematic phase [55, 57]:

$$\begin{aligned} U(1,2) \simeq -\frac{G}{r_{12}^6} - \frac{1}{r_{12}^6} J_1(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)^2 - \frac{1}{r_{12}^6}\{ J_2[(\boldsymbol{u}_1 \cdot \boldsymbol{u}_{12})^2 + (\boldsymbol{u}_2 \cdot \boldsymbol{u}_{12})^2] \\ + J_3[(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_{12})(\boldsymbol{u}_2 \cdot \boldsymbol{r}_{12})]\} \end{aligned} \tag{152}$$

where G describes the isotropic attraction and the constants J_1, J_2 and J_3 describe the anisotropic contribution to the pair interaction potential and depend on the anisotropy of the molecular shape. Following previous discussion, we know that a more precise description of the intermolecular interaction has to include higher order Legendre's polynomials such as the P_4 terms [56], but such terms are usually sufficiently small to be ignored in our model. J_2 accounts for the different interaction energies corresponding to different orientation configurations of the two molecules. For instance for long rods, J_2 has to be negative since the orientation configuration is not energetically favourable, and likewise positive for disc-like molecules. The most important weakness of the model (152) is its uniform r_{12}^{-6} dependence on molecular separation. We shall see that the specific form of this power law is truly irrelevant, since the dominant contribution to the final integrals is arising from the potential cutoff at the molecular excluded volume cutoff. However, particular dependence on the molecular thickness (the closest approach distance) may not be captured accurately in such a model.

2. *Excluded volume effects*: these effects are determined by hard-core repulsion that does not allow molecules to penetrate each other. It is interesting to note that by doing so we

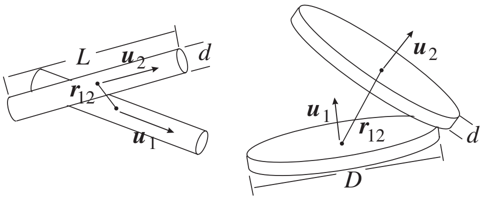

Figure 4. The scheme of excluded volume modelling for rod-like and disc-like particles, leading to the orientation dependent expression for the minimal distance separating the two centres of mass, $\xi_{12}(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_{12})$ of equation (155). The analogous expression for two rods would read $\xi_{12} = d + \frac{1}{2}(L - d)\left[(\boldsymbol{u}_1 \cdot \boldsymbol{u}_{12})^2 + (\boldsymbol{u}_2 \cdot \boldsymbol{u}_{12})^2\right]$ and has a minimum ($\xi_{12} = d$) when both $\boldsymbol{u}_1$ and $\boldsymbol{u}_2 \perp \boldsymbol{u}_{12}$.

already go beyond the formal mean-field approximation, since at low densities it is possible to express the free energy of the system in the form of the virial expansion [59]:

$$\beta F = \rho \ln \rho + \rho \int w_1(\boldsymbol{u}_1)[\ln w_1(\boldsymbol{u}_1) - 1]\, \mathrm{d}\boldsymbol{u}_1 \\ + \frac{1}{2}\rho^2 \int w_1(\boldsymbol{u}_1) w_1(\boldsymbol{u}_2) \cdot B(\boldsymbol{u}_1, \boldsymbol{u}_2)\, \mathrm{d}\boldsymbol{u}_1\, \mathrm{d}\boldsymbol{u}_2 + \cdots \tag{153}$$

where $B(\boldsymbol{u}_1, \boldsymbol{u}_2)$ is the excluded volume for the two particles:

$$B(\boldsymbol{u}_1, \boldsymbol{u}_2) = \int \mathrm{d}\boldsymbol{r}_{12} (\mathrm{e}^{-\beta U_{\text{steric}}(1,2)} - 1) \tag{154}$$

and $U_{\text{steric}}(1, 2)$ is the steric repulsion potential.

In equation (153) all terms are purely entropic in origin since the system is athermal by definition. The second term is the additional orientational entropy which is a consequence of the anisotropic shape of the rigid bodies, and are thus absent in an isotropic liquid. The third term is the packing entropy that can be thought of intuitively as a result of the excluded volumes effects that restrict the molecular motion and therefore reducing the total entropy of the liquid. At low volume fraction of the particles, the higher order terms in the expansion can be neglected. The steric repulsion potential is equivalent to introducing a steric cut-off length. For two disc-like molecules this can be expressed phenomenologically as the distance between COM's when the two particles are in contact:

$$\xi_{12} = D + \frac{(d - D)}{2}[(\boldsymbol{u}_1 \cdot \boldsymbol{u}_{12})^2 + (\boldsymbol{u}_2 \cdot \boldsymbol{u}_{12})^2], \tag{155}$$

where d and D are the thickness and diameter of the discs respectively, and $\boldsymbol{u}_{12}$ is the unit vector along molecular separation line, $\boldsymbol{u}_{12} = \boldsymbol{r}_{12}/|\boldsymbol{r}_{12}|$. The expression can be checked by considering the extreme limits of the molecular directors being parallel or perpendicular to the intermolecular unit vector $\boldsymbol{u}_{12}$. For instance, the shortest separation, $\xi_{12} = d$ is achieved when $\boldsymbol{u}_1 \| \boldsymbol{u}_2 \| \boldsymbol{u}_{12}$.

3. *Three-particle correlation functions*: the simplest form of the three-particle angular distribution function in equation (145) can be expressed in the Kirkwood approximation [1], which neglects three-body collisions:

$$W_3(1, 2, 3) \simeq W_2(1, 2) W_2(2, 3) W_2(1, 3). \tag{156}$$

Such approximation are known to work well at short and long ranges, but is less accurate at a medium range of separation. For a long-rod system, its has been shown by Onsager [59] that virial coefficients higher than second order vanish in the asymptotic limit as the length of the rod goes to infinity. This means that higher order correlations such as the three-body correlations are negligible, and the Kirkwood's approximation is a good limit for infinitely long rods system. Such may not be the case for a discotic phase, when three-body correlations have to be taken into account [58]. One might envisage the use of a better approximation scheme using integral equations such as the Percus–Yevick or Hyper-Netted Chain approximations.

For simplicity we neglect the three-particle collisions, which gives

$$W_3(1,2,3) \simeq \mathrm{e}^{-\beta U(1,2)}\,\mathrm{e}^{-\beta U(1,3)}\,\mathrm{e}^{-\beta U(2,3)} w(\boldsymbol{u}_1) w(\boldsymbol{u}_2) w(\boldsymbol{u}_3) \tag{157}$$

where $w(\boldsymbol{u}_i)$ is the single-particle equilibrium orientation distribution function for molecule i, and $\beta = 1/kT$ as usual.

We return to the evaluation of the integral in equation (145). We first change the variables from $\mathrm{d}\boldsymbol{r}_1$, $\mathrm{d}\boldsymbol{r}_2$ and $\mathrm{d}\boldsymbol{r}_3$ to $\mathrm{d}\boldsymbol{r}_{12}$, $\mathrm{d}\boldsymbol{r}_{13}$ and $\mathrm{d}\boldsymbol{r}_1$. The integrand can be expressed in terms of $\boldsymbol{r}_{12}$ and $\boldsymbol{r}_{13}$ only, which can be integrated over $\boldsymbol{r}_{12}$ and $\boldsymbol{r}_{13}$ (only the relevant terms are shown):

$$\int \frac{1}{r_{12}^4 r_{13}^4} \exp\left\{\frac{k(1,2)}{r_{12}^6} + \frac{k(1,3)}{r_{13}^6} + \frac{k(2,3)}{|\boldsymbol{r}_{13} - \boldsymbol{r}_{12}|^6}\right\} \mathrm{d}r_{12}\,\mathrm{d}r_{13} \tag{158}$$

where

$$\begin{aligned} k(1,2) = \beta\{&G + J_1(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)^2 + J_2[(\boldsymbol{u}_1\cdot\boldsymbol{u}_{12})^2 + (\boldsymbol{u}_2\cdot\boldsymbol{u}_{12})^2] \\ &+ J_3[(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)(\boldsymbol{u}_1\cdot\boldsymbol{u}_{12})(\boldsymbol{u}_2\cdot\boldsymbol{r}_{12})]\}, \quad \text{etc.} \end{aligned} \tag{159}$$

The integrand clearly approaches a maximum towards the cutoff length $r_{12} = \xi_{12} = d$, $r_{13} = \xi_{13} = d$. From equation (155) this requires all the molecular axes to be parallel to intermolecular vectors $\boldsymbol{u}_{12}$, $\boldsymbol{u}_{13}$ and $\boldsymbol{u}_{23}$. If we take small deviations from this conformation only, and $\boldsymbol{u}_{12}$ being in the middle between $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ etc, then equation (159) simplifies to terms containing only two constants, $\tilde{G} = G + \frac{1}{2}J_2 + \frac{1}{4}J_3$ and $\tilde{J} = J_1 + \frac{1}{2}J_2 + \frac{1}{4}J_3$. Equation (145) can be evaluated approximately by observing the sharp rise of the integrand at the end of the integration interval. We therefore obtain

$$\begin{aligned} \langle\xi^2(0)\rangle \approx{}& \frac{(kT)^2}{6d^3}\tilde{J}^2\,\mathrm{e}^{3\beta\tilde{G}} \int \mathrm{d}\boldsymbol{u}_1\,\mathrm{d}\boldsymbol{u}_2\,\mathrm{d}\boldsymbol{u}_3 \\ &\cdot \frac{\partial_1(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)^2 \partial_1(\boldsymbol{u}_1\cdot\boldsymbol{u}_3)^2\,\mathrm{e}^{\beta\tilde{J}[(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)^2 + (\boldsymbol{u}_1\cdot\boldsymbol{u}_3)^2 + (\boldsymbol{u}_2\cdot\boldsymbol{u}_3)^2]} w(\boldsymbol{u}_1) w(\boldsymbol{u}_2) w(\boldsymbol{u}_3)}{[2\tilde{G}' + \tilde{J}'(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)^2 + \tilde{J}'(\boldsymbol{u}_2\cdot\boldsymbol{u}_3)^2][3\tilde{G}' + 2\tilde{J}'(\boldsymbol{u}_1\cdot\boldsymbol{u}_3)^2 + \tilde{J}'(\boldsymbol{u}_2\cdot\boldsymbol{u}_3)^2]} \end{aligned} \tag{160}$$

where $\tilde{G}' = \tilde{G}/d^6$ and $\tilde{J}' = \tilde{J}/d^6$ have the dimensionality of energy.

The equilibrium single-particle orientation distribution function $w(1)$ is proportional to the mean-field nematic potential $U(\boldsymbol{n}\cdot\boldsymbol{u}_1)$, where

$$U(\boldsymbol{u}_1\cdot\boldsymbol{n}) = \int U(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{r}_{12}) w(\boldsymbol{u}_2\cdot\boldsymbol{n})\,\mathrm{d}\boldsymbol{r}_{12}\,\mathrm{d}\boldsymbol{u}_2. \tag{161}$$

That is, the mean-field potential experienced by the first molecule is just the pair interaction energy averaged over the position and orientation of the second molecule. For the discotic nematic phase with interaction energy defined in equation (152) we obtain the mean-field potential with the Maier–Saupe form:

$$U(\boldsymbol{u}_1\cdot\boldsymbol{n}) \approx \text{const} - \frac{4\pi}{9d^3}(2J_1 + J_3) S_2 (\boldsymbol{u}_1\cdot\boldsymbol{n})^2. \tag{162}$$

Equation (160) can be evaluated using again the saddle-point approximation. The integrand possesses a clear maximum point when all molecular axes $\boldsymbol{u}_1$, $\boldsymbol{u}_2$ and $\boldsymbol{u}_3$ are (i) parallel to each other and (ii) aligned parallel to the average macroscopic director $\mathbf{n}$. Another simplification derives from the fact that the anisotropic contribution to the pair potential is usually much smaller than the isotropic contribution $I_1 \ll G$ [55]. With these in mind we obtain a final estimate for the microscopic rotational friction constant $\lambda_\perp$:

$$\lambda_\perp \approx C\sqrt{\frac{I_\perp}{kT}}\exp\left\{\frac{3(\tilde{G}' + \tilde{J}')}{2kT}\right\} \tag{163}$$

where the constant C contains a few microscopic parameters that are not of interest to us. The crucial result from the above analysis is the Arrhenius dependence with the activation energy which corresponds to overcoming the nematic barrier given by the isotropic potential $\tilde{G}'$ and the much weaker anisotropic correction $\tilde{J}'$ during ensemble averaging. The factor $\sqrt{I_\perp/kT}$ takes into account the time averaging process. To summarize the main facts reviewed in this section as follows.

(1) Due to the gyroscopic effects, the discs exhibit more complicated form of velocity correlation function. The dynamical evolution of the particle rotation exhibit multiple time-scales, but its rotational Brownian motion time is described predominantly by the ratio of the moment of inertia to the rotational frictional constant.

(2) The microscopic friction coefficient shows an exponential temperature dependence with a large activation energy determined mainly by the isotropic part of the interaction potential. This seems to account for the observed temperature variation of the Leslie coefficients [60]. Incorporating orientational correlation effects generates a more precise mean-field potential which can be determined self-consistently via numerical methods. One can foresee higher order correlations such as three-body or four-body correlation effects to render even more accurate results and an improved approximation for the friction constant and the Leslie coefficients.

6. Spatially inhomogeneous nematic order

In this section, we consider the effects of spatial inhomogeneities by incorporating the distortions of nematic order using a non-local nematic potential. In the limit of weak flow and mild distortions, this reveals the microscopic origin of the Ericksen stress in the complete Leslie–Ericksen theory. This also provides a new, kinetic, approach to nematic curvature elasticity and gives the microscopic expressions for Frank elastic constants.

The original LE theory assumes that the molecules have a short relaxation time so that their orientation distribution always retains its uniaxial equilibrium ‘shape’, while the local axis of symmetry gets rotated by the flow. The rotational dynamics of the nematics is then characterized by the local director $\boldsymbol{n}$ and the constant order parameter. However, it seems inevitable that at a higher shear rate, the flow may induce significant gradients in the continuous director field and creates spatial inhomogeneities or textures in the sample. In this case, the orientation distribution may be distorted by flow into a non-uniaxial configuration, and the formulation of stress tensor in director variable may not be feasible. Instead, a more adequate formalism [53, 61] will be to consider the dynamics of nematics in terms of the evolution of order parameter tensor as in equation (80).

Another circumstance where distortional effects might become important arise in nematics ridden with defects such as disclination lines and point defects which may be generated due to shear flow. An even more common situation arises due to anchoring condition, when the director field near the surface is forced to align with the walls. This disrupts the molecular packing and incurs a free energy penalty, the minimization of which determines the equilibrium or static dependence of $\boldsymbol{n}(\boldsymbol{r})$. Indeed, the neglect of such distortional stress leads to failures to account for rheological properties of liquid crystalline polymers with domain structures. It was shown that the microscopic theory described so far predicts the formation of disclinations due to inhomogeneous director tumbling which are however constantly annihilated and reformed [53]. Clearly, without distortional elasticity, one cannot describe the defects of nematic order and eventually explain a steady-state network of disclinations, which seems to arise in reality.

Most attempts to account for the distortional elasticity were based on phenomenological models. After the original formulation of the Ericksen stress, Edwards and Beris [62] constructed an ad hoc general expression of Frank elasticity in tensorial form. More recently Tsuji and Rey [61] added distortional energy using the Landau–de Gennes free energy to the kinetic equation but their work does not discuss the stress tensor. Furthermore the use of Landau–de Gennes energy expansion proves to be doubtful for systems with moderately high-order parameters typical of a nematic liquid crystal. This highlights the necessity of a molecular theory. In this section, we demonstrate that by using a non-local nematic potential to model the effects of distortional elasticity, we can derive a new stress tensor and kinetic equation governing the time evolution of the order parameter tensor. The final results are consistent with the complete LE theory in the limit of weak flow and small distortions.

6.1. Ericksen stress

In contrast to a globally uniform director field, a positional variation in the director $\boldsymbol{n}(\boldsymbol{r})$ introduces new distortion free energy in the system which tends to minimize the spatial gradient of the director. The result is an additional contribution to the stress known as the Ericksen stress [43]. In the usual small-motion approximation, this distortional stress gives rise to second-order spatial deviations of $\boldsymbol{n}$ which can be discarded in the formulation of stress tensor. This picture however breaks down at a sufficiently strong shear flow when the local variation in $\boldsymbol{n}$ becomes non-vanishing. Before we embark on a microscopic description of this new effects, we shall first give a brief outline of the definitions of Frank elastic energy and the Ericksen stress.

The classical expression for the distortion free energy takes the following form [43]

$$F_d = \tfrac{1}{2}K_1(\nabla\cdot\boldsymbol{n})^2 + \tfrac{1}{2}K_2(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + \tfrac{1}{2}K_3(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2 \tag{164}$$

where the Frank (curvature elasticity) constants K_i $(i = 1, 2, 3)$ are associated with the three basic types of deformation: splay, bend and twist. For simplicity, we now make a useful one-constant approximation: $K_1 = K_2 = K_3 = K$. The free energy then takes the form

$$F_d = \tfrac{1}{2}K\{(\nabla\boldsymbol{n})^2 + (\nabla\times\boldsymbol{n})^2\} = \tfrac{1}{2}K(\nabla_\alpha n_\beta)(\nabla_\alpha n_\beta) \tag{165}$$

after integration by parts in which we assumed that the surface terms are unimportant in this analysis. Note that this, as well as the one-constant approximation above, are serious limitations; we only adopt them here to preserve clarity of arguments and ideas, as well as make closer contact with the classical de Gennes' monograph (which also follows this route). We can consider a small change in the total free energy δF_{tot} due to a local change in the director, and a material distortion of the fluid which leaves the director orientation invariant [43]. Any changes in the system may be decomposed into these independent changes.

1. *Variation in embedded order*: consider the variation $\boldsymbol{n}(\boldsymbol{r}) \to \delta\boldsymbol{n}(\boldsymbol{r})$, at a fixed point in space, which produces a change in the free energy

$$\delta F_d = \int \left\{ \frac{\partial F}{\partial n_\beta}\delta n_\beta + \frac{\partial F_d}{\delta(\partial_\alpha n_\beta)}\partial_\alpha(\delta n_\beta) \right\} \mathrm{d}\boldsymbol{r}. \tag{166}$$

Integrate the second term by parts and neglect the surface term

$$\delta F_d = \int \left\{ \frac{\partial F}{\partial n_\beta} - \nabla_\alpha\left(\frac{\partial F_d}{\delta(\nabla_\alpha n_\beta)}\right) \right\} \delta n_\beta \,\mathrm{d}\boldsymbol{r}. \tag{167}$$

We can define the terms in the bracket as a molecular field

$$h_\beta = -\frac{\partial F_d}{\partial n_\beta} + \partial_\alpha \pi_{\alpha\beta}, \qquad \text{where} \qquad \pi_{\alpha\beta} = \frac{\delta F_d}{\delta(\partial_\alpha n_\beta)} = \frac{\delta F_d}{\delta g_{\alpha\beta}}. \tag{168}$$

Equation (168) implies that in equilibrium (in the absence of external fields), δF_d must vanish and the director must be at each point parallel to the molecular field.

2. *Material distortion*: we now consider a distortion of the material which preserves the value of the director $\boldsymbol{r} \longrightarrow \boldsymbol{r}' = \boldsymbol{r} + \varepsilon(\boldsymbol{r})$ with $\boldsymbol{n}'(\boldsymbol{r}') = \boldsymbol{n}(\boldsymbol{r})$. The change in the free energy then becomes

$$\delta F_d = \int \sigma^d_{\alpha\beta} \partial_\beta \varepsilon_\alpha \, \mathrm{d}\boldsymbol{r}, \qquad \text{where} \qquad \sigma^d_{\alpha\beta} = -\pi_{\alpha\gamma} \partial_\beta n_\gamma \tag{169}$$

is the distortion stress tensor. If we impose the incompressibility condition for the fluid, we have to introduce a Lagrange multiplier, the pressure p, then the Ericksen stress tensor arises as a result:

$$\sigma^e_{\alpha\beta} = \sigma^d_{\alpha\beta} - p\delta_{\alpha\beta}. \tag{170}$$

Using the one-constant approximation and substituting equation (165) into (168), we have the full stress tensor acting on the element of nematic fluid,

$$\sigma_{\alpha\beta} = \sigma^e_{\alpha\beta} + \sigma^v_{\alpha\beta} = -K \nabla_\alpha n_i \nabla_\beta n_i + \sigma^v_{\alpha\beta} \tag{171}$$

where $\sigma^v_{\alpha\beta}$ is the viscous stress given by equation (47), and the symmetric Ericksen stress is written in the limit of isotropic curvature (Frank) elasticity. One of the aims of this section is to demonstrate that this term can be accounted for by a suitable microscopic theory, and derive an approximate microscopic expression for the Frank constant K.

6.2. Kinetic equation with distortions

One can extend the original theory to include distortional energy. We expect modifications to two major components of the theory: the kinetic equation and the microscopic stress tensor. For a nematic with distorted director configurations, one could consider an additional non-local nematic potential, as proposed by Marrucci and Greco [63]. This potential accounts for spatial variations of the molecular orientation distribution, and represents the molecular interaction energy in a gradually varying orientational mean-field. The effective nematic potential in the presence of spatial inhomogeneities therefore consists of the Maier–Saupe mean-field potential *and* the Marrucci–Greco nematic potential U_{MG} :

$$\tilde{U}(\boldsymbol{u}) = U_{MS} + U_{MG} = -\tfrac{3}{2} J S_{ij} u_i u_j - \tfrac{1}{16} J L^2 \nabla^2 S_{ij} u_i u_j \tag{172}$$

where J is a non-dimensional constant representing the nematic mean-field strength. L denotes the characteristic length-scale for molecular interaction. S_{ij} is the order parameter tensor defined in equation (80). This expression of modified Maier–Saupe potential is a generalized version of the earlier and more familiar equation (88), which applies to the spatially homogeneous case [19, 63]. Here U_{MG} takes care of distortion over the neighbourhood of the molecule, and it can be derived in the limit of small distortion expansion.

Note that we have chosen to write the potential in second-order tensorial form since its relation to the stress tensor can be established more easily. This approach is completely equivalent to our microscopic theory using the distribution function discussed in previous sections. From our kinetic equation (68), we see that the Marrucci–Greco potential generates an additional term:

$$\alpha^2 \int \partial_k \left(w \frac{\partial_k U_{MG}}{kT} \right) \left(u_i u_j - \frac{1}{3}\delta_{ij} \right) \mathrm{d}\boldsymbol{u}$$

$$= \alpha^2 \frac{J L^2}{8kT} (\nabla^2 S_{i\alpha} \langle u_\alpha u_j \rangle + \langle u_i u_\alpha \rangle \nabla^2 S_{\alpha j} - 2\nabla^2 S_{\alpha\beta} \langle u_\alpha u_\beta u_i u_j \rangle). \tag{173}$$

6.3. Nonlocal stress tensor and curvature elasticity

A natural approach to find the modified stress tensor is to return to equation (64). We see that the U_{MG} term generates an additional stress due to distortions:

$$\begin{aligned}\rho\left\langle\frac{p^2}{p^2+1}u_\alpha\frac{\partial U_{MG}}{\partial u_\beta}-\frac{1}{p^2+1}u_\beta\frac{\partial U_{MG}}{\partial u_\alpha}-\tilde{p}u_\alpha u_\beta u_m\frac{\partial U_{MG}}{\partial u_m}\right\rangle\\ =-\frac{1}{8}\rho JL^2\left(\frac{p^2}{p^2+1}S_{i\alpha}\nabla^2 S_{i\beta}-\frac{1}{p^2+1}S_{i\beta}\nabla^2 S_{i\alpha}-\tilde{p}\langle u_\alpha u_\beta u_i u_j\rangle\nabla^2 S_{ij}\right).\end{aligned} \tag{174}$$

Following our earlier approach, we take the symmetric part of this contribution and discover that it can be related to equation (174). This can be written explicitly in terms of the velocity gradient and gives the symmetric part of the viscous stress tensor. This approach however generates no additional terms which can account for the symmetric Ericksen stress $K\nabla_\alpha n_i\nabla_\beta n_i$ in equation (171). We conclude that this straightforward approach does not give a self-consistent microscopic theory that can account for the Ericksen stress, and a more elaborate formalism is required to evaluate the microscopic stress tensor.

Considering that the Ericksen stress can be regarded as an elastic stress due to distortions, we can invoke the principle of virtual work [23], and calculate the elastic stress $\sigma^E_{\alpha\beta}$ from the reaction of the nematic to a rapid virtual deformation $\delta\varepsilon_{\alpha\beta}(\boldsymbol{r})$.

$$\delta F=\int_v \sigma^E_{\alpha\beta}\delta\varepsilon_{\alpha\beta}\,\mathrm{d}V \tag{175}$$

where V is the volume of the bulk sample. By calculating the change in the free energy, we can extract the elastic stress.

The free energy of the nematic liquid crystal can be written in terms of the molecules orientation distribution function $w(\boldsymbol{u})$:

$$F=\rho\int_v \mathrm{d}V\int \mathrm{d}\boldsymbol{u}(kTw\ln w+w\tilde{U}). \tag{176}$$

This gives

$$\delta F=\rho\int_v \mathrm{d}V\int \mathrm{d}\boldsymbol{u}\,[kT\delta w\ln w+kT\delta w+\delta(wU_{MS})+\delta(wU_{MG})]\,. \tag{177}$$

We only have to concern ourselves with the U_{MG} term, since the other terms produce exactly the same microscopic stress tensor as given in equation (64). We therefore have

$$\begin{aligned}\delta F_{MG}&=\rho\int_{\mathrm{v}}\mathrm{d}V\int\delta\,(wU_{MG})\,\mathrm{d}\boldsymbol{u}\\ &=-\frac{\rho JL^2}{16}\int_{\mathrm{v}}\mathrm{d}V\int\delta(w\nabla^2 S_{ij}u_i u_j)\,\mathrm{d}\boldsymbol{u}\\ &=-\frac{\rho JL^2}{16}\int_{\mathrm{v}}\mathrm{d}V\delta(\nabla^2 S_{ij}S_{ij})\\ &=-\frac{\rho JL^2}{16}\int_{\mathrm{v}}\mathrm{d}V(\nabla^2 S_{ij}\delta S_{ij}+\delta\nabla^2 S_{ij}S_{ij}).\end{aligned} \tag{178}$$

The term $\delta\nabla^2 S_{ij}$ represents the energy for additional spatial distortions due to the strain field. This can be calculated explicitly to give

$$\begin{aligned}\delta\nabla^2 S_{ij}&=\left(\frac{\partial\nabla^2 S_{ij}}{\partial t}+\boldsymbol{v}\cdot\nabla\nabla^2 S_{ij}\right)\delta t=\nabla^2\delta S_{ij}+\boldsymbol{v}\cdot\nabla\nabla^2 S_{ij}\delta t\\ &=\nabla^2\delta S_{ij}-\delta\varepsilon_{\alpha\beta}\nabla_\alpha\nabla_\beta S_{ij}-\nabla_\alpha\delta\varepsilon_{\alpha\beta}\nabla_\beta S_{ij}\end{aligned} \tag{179}$$

where we have used integration by parts and neglecting the surface terms. Integrating by parts again we have

$$\int \left(\delta\nabla^2 S_{ij}\right) S_{ij}\,\mathrm{d}V = \int \mathrm{d}V\,(\nabla^2 S_{ij}\delta S_{ij} - \delta\varepsilon_{\alpha\beta}\nabla_\alpha\nabla_\beta S_{ij}S_{ij} + \delta\varepsilon_{\alpha\beta}A_{\alpha\beta}) + \int_\Sigma \mathrm{d}S_\alpha(\nabla_\alpha\delta S_{ij}S_{ij} - \nabla_\alpha S_{ij}\delta S_{ij} - \delta\varepsilon_{\alpha\beta}\nabla_\beta S_{ij}S_{ij})$$

where $A_{\alpha\beta} = \nabla_\alpha S_{ij}\nabla_\beta S_{ij}$, and the contribution to the virtual work

$$\delta F_{MG} = -\frac{\rho J L^2}{16}\left\{\int \mathrm{d}V\,(2\nabla^2 S_{ij}\delta S_{ij} - \delta\varepsilon_{\alpha\beta}\nabla_\alpha\nabla_\beta S_{ij}S_{ij} + \delta\varepsilon_{\alpha\beta}A_{\alpha\beta}) + \int_\Sigma \mathrm{d}S_\alpha(\nabla_\alpha\delta S_{ij}S_{ij} - \nabla_\alpha S_{ij}\delta S_{ij} - \delta\varepsilon_{\alpha\beta}\nabla_\beta S_{ij}S_{ij})\right\}. \tag{180}$$

The surface integral can be put to zero since $\delta\varepsilon$, δS_{ij} and $\nabla\delta S_{ij}$ vanish on the surface boundary.

The variation in the order parameter tensor S_{ij} can be calculated from the kinetic equation (68) by neglecting the diffusion and potential terms for a rapid virtual deformation [23]. In this case,

$$\delta w = \frac{\partial w}{\partial t}\delta t = -\alpha\partial_k(\Omega_k w)\delta t \tag{181}$$

where $\boldsymbol{\Omega} = \frac{1}{2}\tilde{p}\boldsymbol{u}\times g^s\cdot\boldsymbol{u} + \frac{1}{2}\boldsymbol{u}\times g^a\cdot\boldsymbol{u}$ is the residue flow field, as before. We then have

$$\delta S_{ij} = \int u_i u_j \delta w\,\mathrm{d}\boldsymbol{u} = \alpha\int \partial_k(u_i u_j)\Omega_k \delta t w\,\mathrm{d}\boldsymbol{u} = \alpha\left\{\frac{\tilde{p}}{2}\delta\varepsilon^s_{im}S_{jm} + \frac{\tilde{p}}{2}\delta\varepsilon^s_{jm}S_{im} - \tilde{p}\delta\varepsilon^s_{nm}\langle u_n u_m u_i u_j\rangle + \frac{1}{2}\delta\varepsilon^a_{im}S_{jm} + \frac{1}{2}\delta\varepsilon^a_{jm}S_{im}\right\} \tag{182}$$

where $\delta\varepsilon^s$ and $\delta\varepsilon^a$ are the symmetric and asymmetric strain tensor respectively. Using these in equation (175), we finally obtain the part of the elastic stress due to distortion only:

$$\sigma^E_{\alpha\beta} = -\frac{\rho J L^2}{8}\left\{\frac{p^2}{p^2+1}S_{\alpha j}\nabla^2 S_{\beta j} - \frac{1}{p^2+1}S_{\beta j}\nabla^2 S_{\alpha j} - \tilde{p}\nabla^2 S_{ij}\langle u_i u_j u_\alpha u_\beta\rangle\right\} - \frac{\rho UkTL^2}{32}(A_{\alpha\beta} - \nabla_\alpha\nabla_\beta S_{ij}S_{ij}). \tag{183}$$

The free energy approach therefore produces nearly identical stress tensor as in equation (174), except with an additional term $-\frac{1}{32}\rho J L^2(A_{\alpha\beta} - \nabla_\alpha\nabla_\beta S_{ij}S_{ij})$ which is symmetric. We shall see that this term possesses the correct symmetry, as the Ericksen stress, and justifies our use of the virtual deformation principle. This approach also shows explicitly that the addition of distortional elasticity introduces non-local effects into the stress tensor, which now depends on position due to the non-homogeneous Marrucci–Greco potential. This situation differs from a uniform nematic liquid crystal when the principle of locality is assumed which means that both the flow and the nematic configurations are homogeneous [23].

We can gain some physical insights by considering the symmetric part of the stress tensor due to Marrucci–Greco potential U_{MG}. From equation (183) this may be written as

$$\sigma^s_{\alpha\beta} = -\frac{\rho J L^2\tilde{p}\alpha}{16}\{S_{\alpha j}\nabla^2 S_{\beta j} + S_{\beta j}\nabla^2 S_{\alpha j} - 2\nabla^2 S_{ij}\langle u_i u_j u_\alpha u_\beta\rangle\} - \frac{\rho J L^2}{32}(A_{\alpha\beta} - \nabla_\alpha\nabla_\beta S_{ij}S_{ij}). \tag{184}$$

The first term on the right-hand side, together with the original Maier–Saupe term in equation (72), can be replaced by the flow term in the kinetic equation (173). The full symmetric stress tensor with distortions then becomes

$$\sigma^s_{\alpha\beta} = -\frac{\rho k T \tilde{p}}{2\alpha^2}\left(\frac{\partial S_{\alpha\beta}}{\partial t} - G_{\alpha\beta}\right) - \frac{\rho J L^2}{32}(A_{\alpha\beta} - \nabla_\alpha \nabla_\beta S_{ij} S_{ij}) \tag{185}$$

where G_{ij} follows from equation (76). Comparing with the full Leslie–Ericksen stress tensor in equation (171) we see that the first term on the right-hand side produces the viscous stress, while the second term must be equivalent to the Ericksen stress. Equation (185) therefore expresses the reaction of the nematic liquid crystal in terms of velocity gradient (as in the original LE theory) *and* the local variation of nematic configurations, which gives rise to non-local nature of the Ericksen stress.

Using the expression for the uniaxial order parameter tensor S_{ij} and assuming that the magnitude of scalar order parameter S_2 is constant, we have

$$\begin{aligned}\nabla_\alpha S_{ij} \nabla_\beta S_{ij} - \nabla_\alpha \nabla_\beta S_{ij} S_{ij} &= \tfrac{8}{3} S_2^2 \nabla_\alpha n_i \nabla_\beta n_i - \tfrac{2}{3} S_2 \nabla_\alpha n_i \nabla_\beta n_i \\ &\quad - \tfrac{4}{3} S_2^2 n_i \nabla_\alpha \nabla_\beta n_i - \tfrac{2}{3} S_2 n_i \nabla_\alpha \nabla_\beta n_i \\ &= 4 S_2^2 \nabla_\alpha n_i \nabla_\beta n_i \end{aligned} \tag{186}$$

where $n_i \nabla_j n_i = 0$ is frequently used and the last line is obtained from integration by parts. It is important to note at this point that in recent years a number of theories have appeared, which examine the additional effects of variation ∇S_2, or leaving the nematic variables in the tensor form, as $S_{ij}(\boldsymbol{r}, t)$ [64]. Clearly, our approach is adaptable for these continuum theories although here we rigidly follow the path towards the LE model. We therefore obtain a microscopic expression for the average Frank constant:

$$K = \tfrac{1}{8} \rho J L^2 S_2^2 \tag{187}$$

in the limit of elastic isotropy (one constant approximation) and assuming a type of Marrucci–Greco distortional potential.

This expression has several attractive features. It depends on the molecular interaction length and the nematic order parameter in the appropriate way. However we would expect that the Frank constant depends on the molecular aspect ratio p and differs in general for discotic or rod-like nematic phase. Evidently this only applies in the limit of elastic anisotropy when $K_1 \neq K_3$. Marrucci and Greco [63] demonstrated that this is a result of assuming that the length of the rods is long compared to the molecular interaction length L. On the other hand if the interaction length is much larger than the molecular length, the ‘interaction neighbourhood’ becomes essentially spherical and the one-constant approximation becomes fairly accurate. We did not attempt here to pursue the more accurate derivation of Frank elasticity from the kinetic theory, firstly because an excellent equilibrium microscopic models already exist [65, 66] and secondly because our limited aim has been the LE theory of viscosity. No doubt this is an interesting possible avenue of new research.

We note that with the incorporation of Ericksen stress, the Leslie stress tensor becomes non-symmetric in general, and hence angular momentum is not conserved in the usual sense. This gives rise to a mean-field torque which is to be expected since the mean-field potential exerts a torque on the molecules when they are forced away by flow. We therefore expect the usual balance of torque equation to be modified [43]:

$$\int \epsilon_{\alpha\mu\rho} \left\{ r_\rho \sigma^e_{\beta\alpha} + n_\rho \pi^e_{\beta\alpha} \right\} \mathrm{d}S_\beta - \int (\boldsymbol{n} \times \boldsymbol{h})_\mu \, \mathrm{d}\boldsymbol{r} = 0. \tag{188}$$

This balance is required for the conservation of the total angular momentum in static equilibrium. The first term on the left-hand side denotes the surface torque due to elastic distortions in the director field $\boldsymbol{h}$ given by equation (168). There are two contributions to the surface torques, one from the Ericksen stress and one deriving from the tensor π. The second term denotes the torque due to viscous processes, where $\boldsymbol{h}$ is given by equation (48). In static equilibrium this term vanishes when the director is aligned parallel to the molecular field, but the total torque becomes non-vanishing due to the surface torque.

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