Induction of orientational order in the isotropic phase of a nematic liquid crystal

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The orientational properties of an isotropic dense liquid composed by anisotropic molecules, such as a liquid crystal in an isotropic phase, is studied. Using a Langevin-like equation it will be shown that the rotational motion of each molecule can be divided in two elements describing two kinds of physical motion. The first describes the Brownian rotational motion and another the coherent rotation induced by the external fields. It will be shown that, even at the isotropic phase, an order parameter describing the mean degree of alignment of the molecules around a given point can be defined. This order parameter also separates the order coming from the coherent motion from the order generated by the anisotropy in the thermal fluctuations. At the end the proposed model is compared with an experiment and it is shown that the coherent motion is enough to explain the experimental results.

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I. INTRODUCTION

Many thermodynamical properties of the nematic liquid crystals (NLC) are direction dependent and, certainly, these macroscopic anisotropies are due to the characteristic microscopic form of its constituents' molecules. One essential property of the nematic phase is that these molecules present long range orientational order [1,2] while, at the isotropic phase, the amplitude of their vibrations becomes so large that any correlation between their orientation decays with distance and any overall orientation disappears. Usually, the nematic alignment may be controlled with changes in the molecular concentration or temperature and, by this procedure, a nematic-isotropic phase transition can be produced [2,3]. Nevertheless, with the aid of an external induction, the isotropic phase of these liquids may exhibit some signals of the characteristic order of the nematic state; electric and magnetic fields, and even a fluid flow, are used to align the molecules of these materials at the isotropic phase.

In this paper the external induction of these molecular alignments on isotropic liquids composed by anisotropic molecules will be studied. We show that they may be understood as a result of two distinct competing causes; the coherent torques provoked by the external fields that, acting on susceptible anisotropic molecules, incite a regular alignment, and the Brownian aleatory fluctuations that look for the destruction of any uniformity. In the last section of this paper we will compare our theoretical results with the case in which a shearing drag is used to induce local order to these systems. Some experimental measurements will be presented and compared with our theoretical achievements.

The competition between the induction of a coherent alignment and the Brownian tendency for chaos may be formulated using any one of the two distinct, but equivalent, approaches; or the Smoluchowski equation or the Langevin equation [4]. The Smoluchowski equation has already been used in the study of the alignment of rigid rod-like polymers in dilute solutions [4] but, up to our knowledge, the case of high concentrated solution, the liquid crystalline solution at isotropic phase, has not been studied. A Langevin formulation will be proposed in this work. The choice for this formulation is due to the fact that some of the resulting equations can be easily interpreted in terms of the usual differential equations of the classical mechanics. Furthermore, the entire formalism can be understood as an extension of the balance of torques equation [1,5–8] to the isotropic phase.

This paper will be divided into three main sections. In the first one a general Langevin's theory describing the alignment of anisotropic molecules in dense fluids will be proposed. In the sequence, this approach will be applied to describe the behavior of the order parameter of an isotropic phase subjected to an external induction of order. Finally, our theory will be specialized to study the alignment induced by a shearing drag [9–12] and the results will be compared with some experimental data.

II. LANGEVIN'S EQUATION FOR THE BROWNIAN MOLECULAR ROTATIONAL MOTION OF NEMATIC LIQUIDS AT THE ISOTROPIC PHASE

A. The Langevin's equation

Let us consider a liquid composed of uniaxial anisotropic molecules at the isotropic phase. Under these circumstances the correlation between the molecular orientations at different points of the sample is so small that any observed orientational order cannot result from the usual thermodynamical stability, but it must be a consequence of some external induction. The aim of this section is to present a theory describing the mechanism by which this externally induced alignment can be realized. It will consider all torques that act on a given molecule: the aleatory torques and viscous forces of the particles that are in the neighborhoods of a molecule will be added to the external forces acting on the particle. The resulting total torque will describe the rotational motion of the particle. To describe the rotation of a molecule it will

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be assumed that the position of its center of mass is irrelevant and that the unique physically important coordinate is the one fixing its orientation, $\hat{u}$, which will be taken as a unitary vector that gives the direction of the molecular anisotropy.

As a consequence of our approach, an expression to every torque that acts on $\hat{u}$ must be considered. Among them, the form to be attributed to the rotational viscosity of a dense liquid is the most challenging one. Here, the same general hypothesis usually assumed for the nematic liquid will be extended to the isotropic phase; the viscosity is determined by the differences of velocities, $\partial_i V_j$, around the positions of the molecule. Furthermore, as usual [1,5], when we consider the symmetric and the antisymmetric parts of the shearing

$$\partial_i V_j = \tfrac{1}{2}\Phi_{ij} + \tfrac{1}{2}\Omega_{ij}, \tag{1}$$

where

$$\Phi_{ij} = \tfrac{1}{2}(\partial_i V_j + \partial_j V_i) \quad \text{and} \quad \Omega_{ij} = \tfrac{1}{2}(\partial_i V_j - \partial_j V_i), \tag{2}$$

we see that a unique term proportional to $\partial_i V_j$ cannot take care of all viscosity coming from the interaction of a molecule with the motion in its neighborhoods. The antisymmetric part Ω_{ij} describes the rotation of the matter around the molecule with angular velocity

$$\vec{\omega} = \vec{\nabla} \times \vec{V} = (\Omega_{yz}, \Omega_{zx}, \Omega_{xy}), \tag{3}$$

and, as the viscosity can only exist when the own rotation of the molecule, $d_t\hat{u}$, is different from the angular velocity of its surroundings, the antisymmetric part of the shearing drag $\partial_i V_j$ must be taken into account through a term with the form

$$\vec{N} = \vec{\omega} \times \hat{u} - \frac{d\hat{u}}{dt}. \tag{4}$$

That, using coordinates components, can be written as

$$N_i = (\vec{\omega} \times \hat{u})_i - \frac{du_i}{dt} = -\left(\Omega_{ij}u_j + \frac{du_i}{dt}\right). \tag{5}$$

By another side, the symmetric part of the shearing, Φ_{ij} cannot be compensated by any rigid motion of the molecule [this is an essential fact for the interpretation of Eq. (9), below]. So, if we suppose that the viscosity of the molecule under rotation is dominated by the linear components, the torque resulting from this viscous process must have the form

$$\Lambda_i = -\gamma_1^{\mathrm{iso}}\left(\Omega_{ij}u_j + \frac{du_i}{dt}\right) - \gamma_2^{\mathrm{iso}}\Phi_{ij}u_j = -\gamma_1^{\mathrm{iso}}\frac{du_i}{dt} - G_{ij}u_j \tag{6}$$

where

$$G_{ij} = \gamma_1^{\mathrm{iso}}\Omega_{ij} + \gamma_2^{\mathrm{iso}}\Phi_{ij} \tag{7}$$

and γ_1^{iso} and γ_2^{iso} are the viscosity coefficients that couple the antisymmetric and symmetric parts of G_{ij} to the differential equation that describes the rotation of the molecules. Of course, these coefficients are analogous to the usual rotational coefficients γ_1^{iso} and γ_2^{iso} of the nematic phase [1]. At the isotropic phase γ_1^{iso} and γ_2^{iso} are local parameters describing the viscous torques acting on the anisotropic molecules.

Now, the interaction between the anisotropic molecule and an external field will be considered. Without loss of generality, we can consider an external magnetic field $\vec{H}$. So, the simplest form to this torque $\vec{F}_H$,

$$(F_H)_i = \chi(\vec{H}\cdot\hat{u})H_i, \tag{8}$$

is the same of the aligned nematic phase, where χ is the magnetic susceptibility.

We will consider now an important effect acting on the molecules at the isotropic phase, the Brownian motion. The particles move in a thermal bath being constantly pushed by the action of random forces, $F_i(t)$, coming from the aleatory nature of its interactions with its neighborhoods. Furthermore, this force must be in accord with the statistical mechanics of the Brownian oscillatory motion of anisotropic particles [4] and, consequently, it must satisfy the usual relations

$$\langle F_i(t)\rangle = 0 \quad \text{and} \quad \langle F_i(t)F_j(t')\rangle = 2\,\delta_{ij}\gamma_1^{\mathrm{iso}}k_BT \quad \delta(t-t'). \tag{9}$$

Observe that the second one of the above equations gives a realization of the fluctuation dissipation theorem (FDT) and that γ_2^{iso} is not present on it. As our theory considers two viscosity coefficients and only one of them, γ_1^{iso}, appears in Eq. (9) one may be puzzled about the role of the other one, γ_2^{iso}, in the FDT. From a practical point of view we can say that, under the assumption of a ''white'' spectrum for the random fluctuations, the form assumed to Eq. (9) leads to a correct expression to the equipartition theorem and this would be enough to justify our choice (see, for example, Ref. [13]). Nevertheless, we can justify the absence of γ_2^{iso} on the FDT with a much more profound argument. Actually, as we will see below, our model is restricted to rotations. Furthermore, as was stated in the sequence of Eq. (5), the symmetric part of $\partial_i V_j$ describes the viscous coherent motions of the neighborhoods of the molecule that acts in such a way to change their molecular shape. Consequently, the coefficient γ_2^{iso} should be related to dissipations coming from the internal molecular vibrations such as those, for example, that appear when longitudinal oscillations are being considered. So, Eq. (9) says that dissipations through these kinds of fluctuations are not being considered by our model and, as we are considering uniaxial molecules, the above assumption allows us to assume that the statistical mean length of the anisotropic axis $\hat{u}$ is fixed. So, we can express the absence of radial fluctuations saying that

$$\langle \hat{u}^2\rangle = \langle \hat{u}_0^2\rangle = 1. \tag{10}$$

To complete the physical elements that must be present in an equation describing the rotation of an anisotropic molecule the inertial term for the molecular rotations must be

included. It is given by $I\ d\hat{W}/dt$, where I is the moment of inertia, per unit volume, for rotations in which the long axis $\hat{u}$ changes its direction, and $\hat{W}=\hat{u}\times d\hat{u}/dt$ is the local angular velocity of $\hat{u}$.

Adding all the above components we obtain

$$I\frac{d\hat{W}}{dt}+\chi(\vec{H}\cdot\hat{u})\hat{u}\times\vec{H}+\gamma_1^{\rm iso}\hat{u}\times\frac{d\hat{u}}{dt}+\gamma_1^{\rm iso}\hat{u}\times\overrightarrow{\Omega\cdot\hat{u}}+\gamma_2^{\rm iso}\hat{u}\times\overrightarrow{\Phi\cdot\hat{u}}-\hat{u}\times\vec{F}=\vec{0}, \tag{11}$$

where $\overrightarrow{\Omega\cdot\hat{u}}$ and $\overrightarrow{\Phi\cdot\hat{u}}$ are notations for the scalar product of the symmetric and antisymmetric tensors Ω_{ij} and Φ_{ij} with the vector $\hat{u}$. Notice that the above equation is similar to the balance of torques equation for the nematic phase [1,5]. The fundamental, and conceptual, difference between them is that the balance of torques equation deals with a thermodynamical situation where the aggregating elastic forces dominate the scenario, leading to a non-null and continuous value to the statistical mean $\hat{n}=\langle\hat{u}\rangle$. Otherwise, in the isotropic phase, the elastic forces become negligible when compared with the action of the random torques $\hat{u}\times\vec{F}(t)$. Essentially, we can say that the difference between the two equations is that in the isotropic phase a Brownian disordering force substituted the elastic aligning interaction between the domains of the nematic liquid.

Now, as $d\hat{W}/dt=\hat{u}\times d^2\hat{u}/dt^2$, this equation can be written as

$$\hat{u}\times\left(I\frac{d^2\hat{u}}{dt^2}+\chi(\vec{H}\cdot\hat{u})\vec{H}+\gamma_1^{\rm iso}\frac{d\hat{u}}{dt}+\gamma_1^{\rm iso}\overrightarrow{\Omega\cdot\hat{u}}+\gamma_2^{\rm iso}\overrightarrow{\Phi\cdot\hat{u}}-\vec{F}\right)=\vec{0}, \tag{12}$$

which leads to

$$I\frac{d^2\hat{u}}{dt^2}+\gamma_1^{\rm iso}\frac{d\hat{u}}{dt}+\hat{\Gamma}\cdot\hat{u}+\beta\hat{u}=\vec{F}. \tag{13}$$

Where β is a constant resulting from the fact that Eq. (12) is formally equivalent to the equation $\hat{u}\times\vec{X}=0$, that implies that $\vec{X}=-\beta\hat{u}$, and the components of $\hat{\Gamma}$ are given by

$$\Gamma_{ij}=\chi H_iH_j+G_{ij}, \tag{14}$$

where G_{ij} is given in Eq. (7).

Let us make some comments about the meaning of the parameter β introduced in the above equation. Notice that Eq. (12) expresses the fact that the forces acting on $\hat{u}$ do not change its length, but only rotate it. Furthermore, due to the form by which β was introduced it is no more than a degree of freedom acquired by the solutions of Eq. (13) when it is imposed that these solutions would also be solutions of Eq. (12). Therefore once the solutions of Eq. (13) are found they would depend on the free parameter β that is free to be adjusted to represent this constraint. In this sense β behaves like a Lagrange multiple of our theory and, due to the form by which it appears in Eq. (13), it could be used to fix the value of the unitary vector $\hat{u}$, $\hat{u}^2=1$. Observe that this condition is not completely equivalent to Eq. (10). Equation (10) comes from our interpretation for the assumed form to the FDT, while the above result follows from the imposition that the balance of torques equation is restricted to the description of rotations. That is, in one of these equations the length of $\hat{u}$ is strictly fixed while in the other it is its corresponding mean value that is fixed. In this paper we will work with the means values of Eq. (13), these two conditions will be used indistinctly.

As Eq. (13) describes the sum of all torques acting on a molecule it will be called by extended balance of torques equation. The presence of the stochastic interaction, $\vec{F}$, and the absence of the elastic term (expressed through spatial derivatives) led us to the conclusion that the field $\hat{u}$ may not have a continuous behavior. So, the orientation of a molecule can only be understood as a statistical parameter that reveals its observable values when some average is performed. In the next section we will show that it is possible to regard the rotational motion described by Eq. (13) as composed of two components, one of them describing the thermal fluctuation characterizing the Brownian motion and another one describing the coherent rotation of the particle provoked by the action of the external fields, Γ_{ij}. The division of the rotation of the particle in these two terms will support all further development presented below.

At the end of this work some mathematical consequences of Eq. (13) have been introduced as an appendix. When necessary we quote these results.

B. Coherent and incoherent rotations

Here, the physical properties of the solutions of Eq. (13) [or Eq. (11)], which describe the rotational movement of the molecule will be studied. The formalism that we will apply to this problem will separate these rotations into two distinct classes; the stochastic rotation due to the aleatory forces given in Eq. (9) and the coherent rotation induced by the action of the external fields contained in $\hat{\Gamma}$. These results can be obtained when the solution of Eq. (13) is written as

$$u_i(t)=u_i^0(t)+\int^t\mathcal{G}^i(t-t')F_i(t')dt', \tag{15}$$

where $u_i^0(t)$ is a solution of the homogeneous part of Eq. (13) and $\mathcal{G}^i(t-t')$ is the Green's function of the differential equation

$$I\frac{d^2\mathcal{G}^i(t)}{dt^2}+\gamma_1^{\rm iso}\frac{d\mathcal{G}^i(t)}{dt}+\sum_{j=1}^{3}\Gamma_j^i\mathcal{G}^j(t)+\beta\mathcal{G}^i(t)=e^i\delta(t). \tag{16}$$

In this paper the sums' rule for repeated indices will not be used, sums will be written explicitly.

Let us now consider the statistical mean $\langle u_i(t)\rangle$ of Eq. (15). Of course,

$$\langle u_i(t)\rangle = \langle u_i^0(t)\rangle + \int^t \mathcal{G}^i(t-t')\langle F_i(t')\rangle dt' = \langle u_i^0(t)\rangle = u_i^0(t), \tag{17}$$

where we have used the relation $\langle F_i(t')\rangle = 0$, given in Eq. (9). So, the stochastic force $\vec{F}(t)$ does not change the general trends of the free motion; in the mean the particle follows the same path that it would have in the absence of $\vec{F}(t)$. Nevertheless, if averages were not performed, a close view of the trajectory of the particle would detect the effect of the thermal agitation; the particle does not rotate continuously, but executes a zigzagging rotation for which $u_i^0(t)$ is the mean value. So, the results of Eq. (17) allow us to substitute the tortuousness line giving the actual orientation of the particle at each instant by a region where its orientation will be found with certitude. Along each direction the size of this region can be evaluated by computing the fluctuation parameter B_i, given by

$$\begin{aligned} B_i &= \langle [u_i(t) - u_i^0(t)]^2\rangle \\ &= \int\int \mathcal{G}^i(t-t_1')\mathcal{G}^i(t-t_2')\langle F_i(t_1')F_i(t_2')\rangle dt_1' dt_2' \\ &= 2\gamma_1^{\mathrm{iso}} k_B T \int [\mathcal{G}^i(t-t')]^2 dt'. \end{aligned} \tag{18}$$

Notice that, as long as the $\mathcal{G}^i(t)$ may be different for the different directions $\vec{e}_i$, the fluctuation parameters B_i may be also different for the different directions. As we will see ahead, these anisotropies in the orientational fluctuations are induced by the external fields Γ_{ij} acting on the system. In the Appendix, Eq. (A20), we have shown that the sum of all of these parameters is given by

$$\sum_i B_i = \sum_{i=1}^3 \frac{k_B T}{\beta + \lambda^i}, \tag{19}$$

where λ^i are the eigenvalues of the operator $\hat{\Gamma}$, defined in Eq. (14). From this equation we see that the size of the thermal oscillations depends on the values assumed by the parameter β. So, the value of β can be fixed through the size of these fluctuations. In order to do this we remember that u_i gives the instantaneous orientation of a rigid molecule. Therefore at any instant it must satisfy the relation

$$\sum_{i=1}^3 u_i^2 = 1. \tag{20}$$

Using Eq. (15) we find

$$\begin{aligned} \sum_{i=1}^3 \langle u_i^2\rangle &= \sum_{i=1}^3 \left\langle \left(u_i^0(t) + \int^t \mathcal{G}^i(t-t')F_i(t')dt' \right) \right\rangle^2 \\ &= \sum_{i=1}^3 u_i^0(t)^2 + \sum_{i=1}^3 B_i \\ &= \sum_{i=1}^3 [u_i^0(t)]^2 + \sum_{i=1}^3 \frac{k_B T}{\beta + \lambda^i}, \end{aligned} \tag{21}$$

where we have used the results of the Appendix, Eq. (A18).

Furthermore, when the external field $\hat{\Gamma}$ is absent the thermal oscillations would completely dominate the vibrations of the molecules and a coherent path would not exist, that is $u_i^0(t) = 0$. Moreover, as λ^i are the eigenvalues of $\hat{\Gamma}$ we would also have $\lambda^i = 0$. So, under these conditions

$$\sum_{i=1}^3 \langle u_i^2\rangle = \sum_{i=1}^3 \frac{k_B T}{\beta} = \frac{3k_B T}{\beta} = 1, \tag{22}$$

which gives

$$\beta = 3k_B T. \tag{23}$$

Hence, as it was explained below Eq. (14), the parameter β could be considered as a variational parameter fixing the value of $\Sigma_{i=1}^3 \langle u_i^2\rangle = 1$. Therefore now every time that β appears we will assume that $\beta = 3k_B T$. Consequently,

$$\sum_{i=1}^3 \langle u_i^2\rangle = \sum_{i=1}^3 [u_i^0(t)]^2 + \sum_{i=1}^3 \frac{k_B T}{3k_B T + \lambda^i} = 1, \tag{24}$$

and

$$\sum_{i=1}^3 [u_i^0(t)]^2 = 1 - \sum_{i=1}^3 \frac{k_B T}{3k_B T + \lambda^i}. \tag{25}$$

Therefore if we separate from the coherent vector u_i^0 its amplitude $\mathcal{A}$ and its direction w_i^0, $\Sigma_{i=1}^3 (w_i^0)^2 = 1$, that is

$$u_i^0 = \mathcal{A} w_i^0, \tag{26}$$

the above relation, Eq. (24), gives for the amplitude $\mathcal{A}$

$$\mathcal{A}^2 = \sum_{i=1}^3 [u_i^0(t)]^2 = 1 - \sum_{i=1}^3 \frac{k_B T}{3k_B T + \lambda^i} = 1 - \sum_{i=1}^3 B_i. \tag{27}$$

Consequently, remembering our previous assertion that when $\hat{\Gamma} = 0$ we would have $\lambda^i = 0$, we conclude that in the absence of an external field we would also have $\mathcal{A} = 0$. Therefore, as expected, only in the presence of an external field will there be a non-null amplitude for the coherent rotation of the molecule.

However, the above equations are not enough to give the direction for the molecular orientation w_i^0 as a function of the time. In order to obtain w_i^0 we notice that Eq. (20) leads to the two following relations,

$$\sum_{i=1}^{3} u_i \frac{du_i}{dt} = 0 \quad \text{and} \quad \sum_{i=1}^{3} \left(u_i \frac{d^2 u_i}{dt^2} + \left(\frac{du_i}{dt} \right)^2 \right) = 0, \quad (28)$$

that when used in Eq. (13) gives

$$\sum_{i=1}^{3} \left\{ -I \left(\frac{du_i}{dt} \right)^2 + \sum_{j=1}^{3} \Gamma_{ij} u_i u_j - u_i F_i(t) + \beta u_i^2 \right\} = 0. \quad (29)$$

This equation is a first integral of the equation of motion, Eq. (13), and as we will show it can be used to give the orientation followed by the coherent rotation of the molecule. But, according to Eq. (15), when $\vec{F} \to 0$ the function u_i is reduced to the description of the coherent rotation u_i^0 of the molecule. So,

$$\sum_{i=1}^{3} \left\{ -I \left(\frac{du_i^0}{dt} \right)^2 + \sum_{j=1}^{3} \Gamma_{ij} u_i^0 u_j^0 + \beta u_i^0 u_i^0 \right\} = 0 \quad (30)$$

is the differential equation that gives the time development of the coherent oscillation, u_i^0. Using $u_i^0 = \mathcal{A} w_i^0$ and $\Sigma_{i=1}^{3} w_i^0 w_i^0 = 1$, we arrive at

$$-I \left(\frac{d\mathcal{A}}{dt} \right)^2 + \sum_{i=1}^{3} \left\{ -I\mathcal{A}^2 \left(\frac{dw_i^0}{dt} \right)^2 + \mathcal{A}^2 \sum_{j=1}^{3} \Gamma_{ij} w_i^0 w_j^0 \right\} + \mathcal{A}^2 \beta = 0. \quad (31)$$

The set given by Eqs. (27) and (31) completely determine the coherent motion induced by the fluid flow; Eq. (27) gives the amplitude of the coherent motion and Eq. (31) gives its direction.

Now, when the external fields $\hat{\Gamma}$ are such that the time variation of its eigenvalues allows us to make $d_t \mathcal{A} = 0$, Eq. (31) becomes

$$\sum_{i=1}^{3} \left\{ -I \left(\frac{dw_i^0}{dt} \right)^2 + \sum_{j=1}^{3} \Gamma_{ij} w_i^0 w_j^0 \right\} + \beta = 0, \quad (32)$$

that, with the external fields always having a small time variation, describes the time evolution of w_i^0.

Finally, we will show that the above approach also separates the energy of the rotational motion in two components; the energy associated with the coherent motion and the energy associated with the thermal fluctuations. To show how this happens let us consider the kinetic energy E_k associated with the oscillation of the molecule

$$E_k = \frac{1}{2} I \sum_{i=1}^{3} \left\langle \left(\frac{du_i}{dt} \right)^2 \right\rangle. \quad (33)$$

Using Eq. (15) we found

$$E_k = \frac{1}{2} I \sum_{i=1}^{3} \left\langle \left(\frac{du_i^0}{dt} + \int \partial_t \mathcal{G}^i(t-t') F_i(t') dt' \right)^2 \right\rangle = \frac{1}{2} I \sum_{i=1}^{3} \left(\frac{du_i^0}{dt} \right)^2 + \frac{1}{2} I \sum_{i=1}^{3} D_i. \quad (34)$$

The first term of this equation gives the energy contained in the coherent rotational motion of the molecule. The second term gives the energy content of the thermal fluctuations. In the Appendix we have shown that

$$\tfrac{1}{2} I \sum_i D_i = \tfrac{3}{2} k_B T \quad (35)$$

which is just the result predicted by the equipartition theorem; $k_B T/2$ for each degree of freedom.

III. THE ORDER PARAMETER

A. Two components in the order parameter

In this section we study how the external fields can induce local order to the orientations of the anisotropic molecules of a liquid. There are some subtle problems associated with a sounding approach for this problem. One of them concerns the obtainment of a proper formulation of the orientational order in the isotropic phase; in the nematic phase the order parameter is a measure of the thermal molecular fluctuations around the director's direction and, as in the isotropic phase the director does not exist, these questions must be carefully handled. We will follow here the same path followed by the formulation of orientational order for a suspension of rodlike polymers [4]; it will be assumed that the anisotropy of the molecules is well described by a unique axis and the tensor giving the orientational order in a point will be given in terms of the mean of directions of the molecules in the neighborhoods of that point. Only when this mean orientation becomes non-null can one can say that, around this point, there is some order. Therefore if we could describe the physics of the orientation of a unique molecule at a point, by an averaging procedure, we will be able to follow the rising of a local net orientation. Naturally, the essential difference between this kind of orientation and the one observed in the nematic phase is that at the nematic phase the order follows from the thermodynamical stability, and in this case it is induced by an external constraint.

Above, we have seen that the external fields contained in $\hat{\Gamma}$ induce a coherent rotational motion of the molecules of the fluid. Here we will see how this coherent motion can be detected by the measurements of the order parameter. If u_i gives the orientation of a molecule in the liquid, the tensor

$$S_{ij} = \langle u_i u_j - \tfrac{1}{3} \delta_{ij} \rangle, \quad (36)$$

describes its mean orientational properties and, when averages are taken, the corresponding order of the sample. In order to develop this approach let us begin by considering the mean of the product $u_i u_j$,

$$\langle u_i u_j\rangle = \left\langle \left(u_i^0(t) + \int \mathcal{G}^i(t-t')F_i(t')dt' \right) \times \left(u_j^0(t) + \int \mathcal{G}^j(t-t'')F_j(t'')dt'' \right) \right\rangle$$
$$= u_i^0(t)u_j^0(t) + B_{ij},$$
$$B_{ij} = \left\{ 2\gamma_1^{\text{iso}} k_B T \int^t [\mathcal{G}^i(t-t')]^2 dt' \right\} \delta_{ij} = B_i \delta_{ij}. \quad (37)$$

From this result it follows that

$$S_{ij} = u_i^0(t)u_j^0(t) - \tfrac{1}{3}(\delta_{ij} - 3B_{ij}). \quad (38)$$

Nevertheless,

$$\frac{1}{3}(\delta_{ij} - 3B_{ij}) = \frac{1}{3}(1-3B_i)\delta_{ij}$$
$$= \frac{1}{3}\left[\left(1 - \sum_{k=1}^{3} B_k \right)\delta_{ij} + \left(\sum_{k=1}^{3} B_k - 3B_i \right)\delta_{ij} \right]$$
$$= \frac{1}{3}\mathcal{A}^2\delta_{ij} + \Delta_{ij}, \quad (39)$$

$$\Delta_{ij} = 3\left[\left(\frac{\sum_k B_k}{3} \right) - B_i \right]\delta_{ij}, \quad (40)$$

where Eq. (27) has been used. Therefore from Eqs. (18) and (26) one obtains

$$S_{ij} = \mathcal{A}^2(w_i^0 w_j^0 - \tfrac{1}{3}\delta_{ij}) + \Delta_{ij}. \quad (41)$$

Along the next sections the meaning of these two terms will be discussed in detail. Evidently, the first one expresses the order induced by the coherent motion and will be called by coherent order parameter. The other term, Δ_{ij}, follows from the anisotropy introduced in the thermal fluctuations by the external fields and will be called by thermal order parameter. As we will see this name is justified by the fact that it is of the order of the thermal fluctuations.

B. Thermal order parameter and the anisotropy on the Brownian fluctuations

Let us consider the thermal order parameter Δ_{ij}. As discussed in the Eq. (18), it comes from the anisotropy provoked on the fluctuation parameter, B_i, by the external fields. That is, in Eq. (39) the term $\Sigma_k B_k/3$ gives the mean of the fluctuations parameters, while the isolated term B_i gives the fluctuations along one fixed direction $\vec{e}_i$. Therefore, the difference, $\Delta_{ij} = 3[(\Sigma_k B_k/3) - B_i]\delta_{ij}$, is a measure for the anisotropy on these fluctuations. In a ''free'' isotropic phase $(\hat{\Gamma} = 0)$ these fluctuations are equal along all directions and we would have $\Delta_{ij} = 0$. Nevertheless, as explained in Eq. (18), an external field introduces anisotropies on B_i leading to a non-null value to Δ_{ij}.

But, joining Eq. (39) with Eqs. (18) and (19) we have

$$\Delta_{ij} = 3\left[\left(\frac{\sum_k B_k}{3} \right) - B_i \right]\delta_{ij}$$
$$= 3k_B T\left(\frac{1}{3}\sum_{k=1}^{3} \frac{1}{3k_B T + \lambda^k} - 2\gamma_1^{\text{iso}} \int [\mathcal{G}^i(t-t')]^2 dt' \right)\delta_{ij}. \quad (42)$$

In order to evaluate this term let us use the bases formed by the eigenvector of Γ_{ij}. Using the results found in the Appendix we have

$$\int dt'[\mathcal{G}^\alpha(t-t')]^2 = \frac{1}{2\ \gamma_1^{\text{iso}}(3k_B T + \lambda^\alpha)}. \quad (43)$$

Therefore

$$\Delta_{\alpha\beta} = 3k_B T\left\{ \frac{1}{3}\sum_{k=1}^{3} \frac{1}{3k_B T + \lambda^k} - \frac{1}{3k_B T + \lambda^\alpha} \right\}\delta_{\alpha\beta}$$
$$= k_B T\left\{ \sum_{k\neq\alpha}^{3} \frac{1}{3k_B T + \lambda^k} - 2\frac{1}{3k_B T + \lambda^\alpha} \right\}\delta_{\alpha\beta}. \quad (44)$$

Notice that, independently of the values assumed by the eigenvalues λ^k, this expression would be of the order of $k_B T$, which characterizes the size of the thermal agitation. In the next section we will show that the coherent order parameter is not proportional to $k_B T$ and, for a realistic system, dominates the order of the system.

C. Coherent order parameter

According to Eq. (41) the coherent order parameter, S_{ij}^0, is given by

$$S_{ij}^0 = \mathcal{A}^2(w_i^0 w_j^0 - \tfrac{1}{3}\delta_{ij}), \quad (45)$$

where $\mathcal{A}^2$ is given by Eq. (27) and w_i^0 is the solution of Eq. (31).

As w_i^0 is time dependent this tensor also is time dependent. For the cases for which w_i^0 has a small rotational frequency this time dependence could be easily detected in experiments. But, in general, the inertial momentum appearing in Eq. (31) is so small that the rotational frequency of w_i^0 becomes so high that the time dependence of Eq. (45) would be undetectable. Furthermore, it is easy to see that the rotational frequency of w_i^0 resulting from Eq. (31) need not be constant. When this happens the molecule does not rotate spending an equal amount of time for all directions; there will be some directions along which it points for more time. However, if the frequency of rotation of the molecule is high enough, the orientations in which the molecule stays for more time may dominate the scenario and in a measurement

some orientational order would be detected. Under these conditions the time average of Eq. (45) would reveal such orientational order. So,

$$\overline{S_{ij}^0}=\langle \mathcal{A}^2(w_i^0 w_j^0-\tfrac{1}{3}\delta_{ij})\rangle_t, \tag{46}$$

where $\langle\chi\rangle_t$ gives the time average of χ.

Usually, the tensor giving the order parameter cannot be directly measured and the order in the system is measured by the scalar that is obtained by the contraction of S_{ij} with the vector giving the direction along which the order is to be detected. So, if we measure the order parameter along the direction

$$\vec{n}=\vec{i}\cos\varphi+\vec{j}\sin\varphi, \tag{47}$$

the scalar

$$\overline{S^0}(\varphi)=\tfrac{3}{2}n_i n_j \overline{S_{ij}^0} \tag{48}$$

measures the coherent order of the system along the direction $\vec{n}$.

D. Symmetric and antisymmetric parts of Γ_{ij}

In the study so far presented the order parameter has been separated into two components. One, accounting for the anisotropy introduced in the fluctuation by the external fields, and another, accounting for coherent motion induced on the molecules by the fluid flow. Now, some symmetrical properties of the operator $\hat{\Gamma}$ will be used to determine the properties of the order parameter.

For example, as we have stressed above only when the time evolution of $\dot{w}_i^0$ is nonuniform is a non-null value for Eq. (45) found. But, according to Eq. (46) the value of $\dot{w}_i^0$ is essentially determined by $\Sigma_{i,j}\Gamma_{ij}w_i^0 w_j^0$. So, a pure antisymmetric tensor Γ_{ij} leads to a zero in this sum, and the orientational order parameter becomes null. That is, this reasoning reveals that the direction of the orientational order parameter, $\overline{S_{ij}^0}$, is fixed by the symmetric part of Γ_{ij}. An important consequence of the above development is that a pure antisymmetric tensor cannot produce any order in the alignment of the molecules.

IV. ORDER INDUCTION WITH THE USE OF FLUID FLOW

A. A bidimensional shearing drag

Now the tensor Γ_{ij} will be restricted to the description of a bidimensional fluid flow. That is, along the direction $\vec{e}_z$ there is not relevant fluid flow, $\partial_z V_i=0$, $i=(x,y,z)$, and the external field H_i is assumed to be null. The advantage of this simplification is that it will furnish an immediate application of our model. For this situation the $\vec{e}_z$ components of the tensor $\Gamma_{ij}=G_{ij}=\gamma_1^{\rm iso}\Omega_{ij}+\gamma_2^{\rm iso}\Phi_{ij}$ becomes $\Gamma_{iz}=0$, $i=(x,y,z)$. So, the solution of Eq. (A9) requires the study of the three-dimensional problem

$$\hat{\Gamma}\cdot\vec{v}^{\alpha}=\lambda^{(\alpha)}\vec{v}^{(\alpha)}, \tag{49}$$

that, save for the trivial solution

$$\lambda^3=0 \quad \text{and} \quad (v_x^3)^2=(v_y^3)^2=(v_z^3)^2=\tfrac{1}{3}, \tag{50}$$

is reduced to the bidimensional problem

$$\begin{bmatrix} \gamma_2^{\rm iso}\Phi_{xx} & \gamma_2^{\rm iso}\Phi_{xy}+\gamma_1^{\rm iso}\Omega_{xy} \\ \gamma_2^{\rm iso}\Phi_{xy}-\gamma_1^{\rm iso}\Omega_{xy} & -\gamma_2^{\rm iso}\Phi_{xx} \end{bmatrix}\begin{bmatrix} v_x \\ v_y \end{bmatrix}=\lambda\begin{bmatrix} v_x \\ v_y \end{bmatrix}, \tag{51}$$

where we have used the continuity equation $\Phi_{xx}+\Phi_{yy}=0$.

As it is being considered a bidimensional flow it can be supposed that the coherent motion of the molecule happens in the plane perpendicular to the plane of the shearing. So,

$$\vec{w}=\vec{i}\cos\theta+\vec{j}\sin\theta, \tag{52}$$

where the time evolution of θ describes the rotation of w_i^0. Using these variables it is found

$$\overline{S^0}(\varphi)=\frac{\mathcal{A}^2}{3}\langle 3\cos^2(\theta-\varphi)-1\rangle_t.$$

In order to obtain the time evolution of θ we use Eq. (32) and obtain

$$I\sum_i\left(\frac{dw_i^0}{dt}\right)^2=\beta+\sum_{i,j}\Gamma_{ij}w_i^0 w_j^0. \tag{53}$$

Using the coordinate system given in Eq. (52) and the incompressibility of the fluid, we obtain

$$I\left(\frac{d\theta}{dt}\right)^2=\beta+\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}\sin 2(\theta+d), \tag{54}$$

where

$$d=\tfrac{1}{2}\arctan(\Phi_{xx}/\Phi_{xy}). \tag{55}$$

These equations give the time evolution of the angular position θ as a function of the shearing drag. As it is suggested at the beginning of this section it is the nonuniformity of $\dot{\theta}$ that will produce an orientational order on the molecules of the sample; during the time the molecules will be found for more time pointing to one direction than to another. This equation is analogous to an equation for the oscillation of a particle in the one-dimensional conservative potential $U(\theta)=-\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}\sin 2(\theta-d)$. From this equation we see that the relative values of $\beta=3k_BT$ and $\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}$ determine the kind of rotational motion of the molecule. Three different regions

$$\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}=0, \quad 0<\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}<3k_BT, \quad \text{and} \quad \sqrt{\Phi_{xx}^2+\Phi_{xy}^2}\geqslant 3k_BT \tag{56}$$

characterize these motions. For $\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}=0$ we would have $\mathcal{A}=0$, therefore, there is not any kind of alignment. For

the second situation the particle rotates assuming all values of θ. But, because there are regions of θ in which the particle stays for more time, some order will be found in this region. Finally, when $\sqrt{\Phi_{xx}^2+\Phi_{xy}^2} \geqslant 3k_BT$, the rotational motion of the particle does not assume all values of θ, and its oscillatory motion becomes restricted to some regions of the domain of θ, existing a clear mean alignment.

In order to compute these time averages, Eq. (54) is used to make

$$dt = \frac{d\theta}{\frac{1}{I}\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}\sqrt{[\varepsilon+\sin 2(\theta+d)]}}, \tag{57}$$

where $\varepsilon = \beta/\sqrt{\Phi_{xx}^2+\Phi_{xy}^2}$. So,

$$\overline{S^0}(\varphi) = \frac{\mathcal{A}^2}{3}\langle 3\cos^2(\theta-\varphi)-1\rangle_t$$

$$= \frac{\mathcal{A}^2}{6}\frac{1}{P(\varepsilon)}\int_R \frac{[3\cos 2(\theta-\varphi)+1]d\theta}{\sqrt{\varepsilon+\sin 2(\theta+d)}}, \tag{58}$$

where

$$P(\varepsilon) = \int_R \frac{d\theta}{\sqrt{\varepsilon+\sin 2(\theta+d)}}, \tag{59}$$

and the index R under the integration symbol means that the integration is restricted to the regions where the square root appearing in Eq. (59) gives a real number.

Making $\chi = \theta + d$, we have

$$\overline{S^0}(\varphi) = \frac{\mathcal{A}^2}{6}\left\{\frac{1}{P(\varepsilon)}\int_R \frac{3\cos 2[\chi-(d+\varphi)]d\chi}{\sqrt{(\varepsilon+\sin 2\chi)}}+1\right\}$$

$$= \frac{\mathcal{A}^2}{6}\left\{3\sin 2(d+\varphi)\frac{1}{P(\varepsilon)}\int_R \frac{\sin 2(\chi)d\chi}{\sqrt{(\varepsilon+\sin 2\chi)}}+1\right\}.$$

This equation gives the general expression for the coherent order parameter. It can be further simplified if we observe that

$$R(\varepsilon) = \frac{1}{P(\varepsilon)}\int_R \frac{\sin 2(\chi)d\chi}{\sqrt{[\varepsilon+\sin 2(\theta+d)]}}$$

$$= -\varepsilon + (1+\varepsilon)\frac{E\left(\phi, \frac{2}{1+\varepsilon}\right)}{F\left(\phi, \frac{2}{1+\varepsilon}\right)}, \tag{60}$$

where $\phi = (1/4)[\pi + 2\arcsin(\varepsilon)]$, $F(\phi,k) = \int_0^\phi d\theta/\sqrt{1-k^2\sin^2\theta}$ is the elliptical integral of first class, and $E(\phi,k) = \int_0^\phi \sqrt{1-k^2\sin^2\theta}d\theta$ is the elliptical integral of second class. So,

$$\overline{S^0}(\varphi) = \frac{\mathcal{A}^2}{6}\{3R(\varepsilon)\sin 2(d+\varphi)+1\} \tag{61}$$

gives, in the geometry discussed above, the temporal mean of the order attributed to the coherent rotation of the molecules.

Let us consider also the amplitude $\mathcal{A}$ of the coherent fluid flow. We will compute it in the planar geometry given by Eq. (52) where the eigenvalues are given by Eqs. (50) and (51), $\lambda = 0$, and $\lambda = \pm\tilde{\lambda}$, therefore,

$$\mathcal{A}^2 = \left(1 - \sum_i \frac{k_BT}{3k_BT+\lambda^i}\right) = \frac{2\tilde{\lambda}^2}{3[\tilde{\lambda}^2 - 9(k_BT)^2]}. \tag{62}$$

So, there are two cases to be considered, $\tilde{\lambda}^2 < 9(k_BT)^2$ and $\tilde{\lambda}^2 > 9(k_BT)^2$. The first case leads to an imaginary amplitude and, as for any realistic system we would have $\tilde{\lambda}^2 \gg 9(k_BT)^2$, it has no physical interest. Consequently, from now on we will assume

$$\mathcal{A}^2 \simeq \tfrac{2}{3}. \tag{63}$$

B. The experiment

According to the theory developed above, external fields may induce order in the alignment of the anisotropic molecules. Furthermore, due to the form of Eq. (61) this order depends on the variables: (a) the direction in which the order is measured, given by the angle φ of Eq. (47); (b) a relation between the symmetric parts of the fluid flow, characterized by the parameter d, given in Eqs. (55) and (2); (c) the global characteristics of the rotational properties of the trajectory followed by the molecule, described by the parameter $R(\varepsilon)$, as defined in Eq. (60); and (d) the amplitude $\mathcal{A}$ of the coherent motion, given by Eqs. (62) and (63). So, in order to test the above theory, its predictions will be compared with the experimental results obtained when a change to some of these variables is done. Observe that there are two classes of parameters. The ones, φ and d, that are connected to the geometry of the experimental arrangement, and the ones, $R(\varepsilon)$ and $\mathcal{A}$, that come from the dynamics of the rotation of the molecules. We hope that when the shearing drag becomes sufficiently high, these last ones become nearly constant as happened, for example, with the amplitude $\mathcal{A}$ in Eq. (63). Hence an easy way to test the validity of the relation given by Eq. (61) is to change progressively the internal geometry of the sample and compare the corresponding experimental results with the predictions of the theory.

In order to perform such an investigation, a vessel filled with potassium laurate, KL (26.89%), decanol, DeOH (6.34%), and water (66.77%), at the isotropic phase, was submitted to a shearing drag due to the falling of a metallic lamina along an inclined plane, put inside the sample. The alignment induced by such shearing drag was obtained through the measurement of the changes in the birefringency along the direction of the gravitational field, $\varphi = \pi/2$. For each measurement the angle, ϕ, between the direction of the motion of the lamina and the gravitational field was changed, while the direction along with the birefringency was measured and remained fixed. This change in the angle of the inclined plane gives to us the geometrical change. The result-

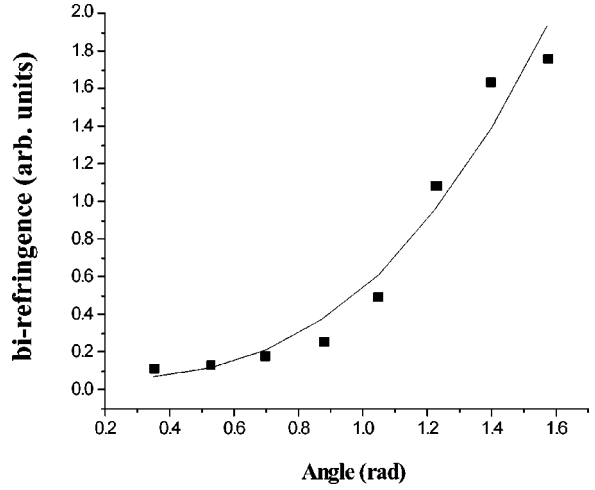

FIG. 1. Birefringency and transmittance as a function of the angle of the inclined plane in which a metallic lamina falls creating a shearing drag. The angle was measured from the horizontal line and arbitrary unities were used in the measurement of the transmittance. The dots represent the points obtained in the measurement and the continuous line gives the results of our model.

ing data for the birefringency, Br, are shown in Fig. 1. The relation between the birefringency and the order parameter is given by the known relation [14]

$$Br = \alpha S^2, \tag{64}$$

where α is a proportionality constant. In this equation the order parameter S is composed of the terms presented in the last section. One comes from the order imposed by the coherent motion and one comes from the anisotropy introduced in the fluctuations by the fluid flow. So,

$$S = \overline{S^0}(\varphi) + \overline{S^\Delta},$$

where $\overline{S^0}(\varphi)$ was defined in Eq. (61) and $\overline{S^\Delta}$ follows from the application of Eq. (48), $\overline{S^\Delta} = 3/2 n_i n_j \Delta_{ij}$, to the thermal order parameter, Eq. (44). Above, it has been shown that the thermal order parameter would be of order of $k_B T$ and therefore it would be small when compared with the coherent of the order parameter. Consequently, the present analysis will be restricted to this last component. So, as the birefringency was measured along the direction of the gravitational field we have $\varphi = \pi/2$, and hence

$$\overline{S^0}(\varphi) = \frac{\mathcal{A}^2}{6}\{-3R(\varepsilon)\sin 2d + 1\}.$$

According to Eq. (55) one has $\sin 2d = \Phi_{xx}/\sqrt{\Phi_{xx}^2 + \Phi_{xy}^2}$. In order to compute the values of these terms we remember that $V_x = V\cos\phi$, and that $\partial_x = \cos\phi\partial_r$. So,

$$\Phi_{xx} = \partial_x V_x = \cos^2\phi\,\partial_r V.$$

Analogously, $V_y = V\sin\phi$, and that $\partial_y = \sin\phi\partial_r$, and

$$\Phi_{xy} = \tfrac{1}{2}(\partial_x V_y + \partial_y V_x) = \tfrac{1}{2}(\cos\phi\sin\phi\partial_r V + \sin\phi\cos\phi\partial_r V)$$
$$= \tfrac{1}{2}\partial_r V \sin 2\phi.$$

Therefore

$$\sin 2d = \frac{\Phi_{xx}}{\sqrt{\Phi_{xx}^2 + \Phi_{xy}^2}} = \frac{\cos^2\phi\partial_r V}{\sqrt{\cos^4\phi(\partial_r V)^2 + \frac{1}{4}\sin^2 2\phi(\partial_r V)^2}}$$
$$= \frac{\cos^2\phi}{\sqrt{\cos^4\phi + \frac{1}{4}\sin^2 2\phi}} = \cos\phi.$$

This is an important relation because it means that the parameter d does not depend on the dynamical parameters of the experiment, such as the velocity V of the fluid. Therefore it is a genuine geometrical parameter. So,

$$\overline{S^0}(\varphi) = \frac{\mathcal{A}^2}{6}\{-3R(\varepsilon)\cos\phi + 1\},$$

but, according to our previous discussion we have

$$B = \alpha S^2 = [\overline{S^0}(\varphi)]^2 = \alpha\left(\frac{\mathcal{A}^2}{6}\{-3R(\varepsilon)\cos\phi + 1\}\right)^2$$
$$= a(-b\cos\phi + 1)^2,$$

where $a = \alpha(\mathcal{A}/6)^2$ and $b = 3R(\varepsilon)$.

In order to compare the results of this theory with the experimental data, shown in Fig. 1, we have looked for the values of a and b that furnish the best adjustment for these data. For our theory the value of the parameter a is immaterial because (a) it contains the parameter α that comes from Eq. (64) that is outside of our model and (b) it is a scale factor and, in the experiment, the birefringency is also measured save a scale factor. So, to adjust the experimental data only the parameter b has physical significance. For the data exhibited in Fig. 1 we have obtained

$$a = 1.92 \quad \text{and} \quad b = 0.87,$$

shown by the continuous line in Fig. 1.

V. CONCLUSION AND PERSPECTIVES

In this work we have presented a theory for the induced alignment of the molecules of the isotropic dense fluids, which at lower temperatures are in the nematic phase. We have applied this theory to the case in which the sample is submitted to a shearing drag and the experimental results agree with theory. An interesting aspect of this approach is that it can be applied to many experimental situations. Along the paper we stressed the action of the external fields and shearing drag, but any kind of action that causes a fluid flow can be coupled to Eq. (13). For example, through the use of the Navier–Stokes equation we can study how the action of

pressure gradients can induce local order in these anisotropic molecules and how this order travels along the sample.

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APPENDIX

Here, the solutions of the differential equation

$$I\frac{d^2\hat{u}}{dt^2}+\gamma_1^{\rm iso}\frac{d\hat{u}}{dt}+\hat{\Gamma}\cdot\hat{u}+\beta\hat{u}=\vec{F} \tag{A1}$$

will be studied.

Let us begin by considering the case in which the external fields $\vec{H}$ and $\hat{G}$ contained in $\hat{\Gamma}$ are considered nulls. Hence this equation becomes

$$I\frac{d^2\hat{u}}{dt^2}+\gamma_1^{\rm iso}\frac{d\hat{u}}{dt}+\beta\hat{u}=\vec{F}. \tag{A2}$$

As the solution of this equation must fulfill the requirement $\Sigma_{i=1}^{3}u_i^2=1$, that means that the motion of u_i happens on the surface of a sphere, it must appear that this is a highly nonlinear differential equation. But, as it was explained along the text, the parameter β is free to be adjusted to fix this condition. Therefore, taking advantage of this degree of freedom, the solution of this equation can be taken as the solution of the damped oscillator.

From Eq. (A2) the Green's functions, $\mathcal{G}_0^i(t)$, are determined by solving the differential equation

$$I\frac{d^2\vec{\mathcal{G}}_0(t)}{dt^2}+\gamma_1^{\rm iso}\frac{d\vec{\mathcal{G}}_0(t)}{dt}+\beta\vec{\mathcal{G}}_0(t)=\vec{\delta}(t). \tag{A3}$$

As in Eq. (15), the index 0 indicates that for this parameter the external fields are not being considered. Furthermore, observe that $\mathcal{G}_0^i(t)$ does not depend on direction; only through the external fields of $\hat{\Gamma}$ is the anisotropy of the external fields introduced in the Green's function. By the usual procedures it can be shown that

$$\mathcal{G}_0^j(t)=\frac{1}{2\pi}\int\frac{d\omega\, e^{i\omega t}}{-I\omega^2+i\gamma_1^{\rm iso}\omega+\beta}\quad\text{for all } j. \tag{A4}$$

Using this equation, the parameter

$$B_0^i=2\gamma_1^{\rm iso}k_BT\int dt'[\mathcal{G}_0^{(i)}(t-t')]^2 \tag{A5}$$

given by Eq. (19) can be computed for $\mathcal{G}_0^i$. It is straightforward to show that

$$\int dt'[\mathcal{G}_0^{(i)}(t-t')]^2=\frac{1}{2\pi}\int\frac{d\omega}{(-I\omega^2+\beta)^2+(\gamma_1^{\rm iso}\omega)^2}$$

$$=\begin{cases}\dfrac{1}{2\beta\gamma_1^{\rm iso}} & \text{if } \beta>0\\[2ex] \pi\sqrt{\dfrac{1}{\beta^2(\gamma_1^2-4I\beta)}} & \text{if } \beta<0.\end{cases} \tag{A6}$$

Likewise, one can show that

$$\int dt'[\partial_t\mathcal{G}_0^{(i)}(t-t')]^2=\frac{1}{2\pi}\int\frac{\omega^2 d\omega}{(-I\omega^2+\beta)^2+(\gamma_1^{\rm iso}\omega)^2}$$

$$=\frac{1}{2\gamma_1^{\rm iso}I}. \tag{A7}$$

Therefore

$$D_0^i=2\gamma_1^{\rm iso}k_BT\int dt'[\partial_t\mathcal{G}_0^{(i)}(t-t')]^2=\frac{k_BT}{I}. \tag{A8}$$

In the computation of the values of B_0^i and D_0^i made above the effect of the external fields, contained in $\hat{\Gamma}$, was not taken into account. In order to consider it, let us suppose that $\hat{\Gamma}$ is time independent or, at least, has a very small time variation. Furthermore, let us suppose that $\hat{\Gamma}$ has a complete set of eigenvalues, λ^{α}, and eigenvectors, $\vec{v}^{\alpha}$, satisfying

$$\hat{\Gamma}\cdot\vec{v}^{\alpha}=\lambda^{(\alpha)}\vec{v}^{(\alpha)}. \tag{A9}$$

So we can make

$$\hat{u}=\sum_{\alpha=1}^{3}u_{\alpha}(t)\vec{v}^{\alpha}\quad\text{and}\quad\vec{F}=\sum_{\alpha=1}^{3}F_{\alpha}(t)\vec{v}^{\alpha}, \tag{A10}$$

where the time dependence is put on the coefficients $u_{\alpha}(t)$ and $F_{\alpha}(t)$. Putting these parameters in Eq. (A2) we obtain

$$\left[I\frac{d^2u_{\alpha}(t)}{dt^2}+\gamma_1^{\rm iso}\frac{du_{\alpha}(t)}{dt}+(\beta+\lambda^{(\alpha)})u_{\alpha}(t)\right]\vec{v}^{\alpha}=F_{\alpha}(t)\vec{v}^{\alpha}. \tag{A11}$$

That leads to the differential equation

$$I\frac{d^2u_{\alpha}(t)}{dt^2}+\gamma_1^{\rm iso}\frac{du_{\alpha}(t)}{dt}+(\beta+\lambda^{(\alpha)})u_{\alpha}(t)=F_{\alpha}(t), \tag{A12}$$

for the direction of the eigenvector $\vec{v}^{\alpha}$. As the eigenvalues $\lambda^{(\alpha)}$ are (presumably) different, the anisotropy of the problem is restored. Furthermore, with the change $\beta+\lambda^{(\alpha)}\rightarrow\beta'$

the differential equations given by Eqs. (A2) and (A12) become formally identical. Therefore, along the directions given by $\vec{v}^{\alpha}$, this differential equation describes forced damped oscillations, where the elastic constants are given by $\beta+\lambda^{(\alpha)}$. In order to obtain the law of transformation for these objects to the base $\vec{e}_i$ we make

$$\vec{v}^{\alpha}=v_i^{\alpha}\vec{e}_i, \tag{A13}$$

but, using Eq. (A10) we have

$$\hat{u}=\sum_{\alpha=1}^{3} u_{\alpha}(t)\vec{v}^{\alpha}=\sum_{\alpha=1}^{3}\sum_{i=1}^{3} u_{\alpha}v_i^{\alpha}\vec{e}_i. \tag{A14}$$

So,

$$u_i=\sum_{\alpha=1}^{3} u_{\alpha}v_i^{\alpha}. \tag{A15}$$

Likewise

$$\mathcal{G}^i(t-t')=\sum_{\alpha=1}^{3} v_{\alpha}^{i}\mathcal{G}^{\alpha}(t-t'). \tag{A16}$$

Furthermore

$$\begin{aligned} u_i^2&=\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}\sum_{i=1}^{3}\sum_{j=1}^{3} u_{\beta}u_{\alpha}v_i^{\beta}v_j^{\alpha}\vec{e}_i\cdot\vec{e}_j\\ &=\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}\sum_{i=1}^{3} u_{\beta}u_{\alpha}v_i^{\beta}v_j^{\alpha}\delta_{ij}\\ &=\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}\sum_{i=1}^{3} u_{\beta}u_{\alpha}v_i^{\beta}v_i^{\alpha}=\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3} u_{\beta}u_{\alpha}\delta_{\alpha\beta}\\ &=\sum_{\alpha=1}^{3}(u_{\alpha})^2. \end{aligned} \tag{A17}$$

From these relations it follows that

$$\sum_i \int dt'[\mathcal{G}^{(i)}(t-t')]^2=\sum_{\alpha}\int dt'[\mathcal{G}^{\alpha}(t-t')]^2 =\sum_{\alpha}\frac{1}{2\gamma_1^{\mathrm{iso}}(\beta+\lambda^{(\alpha)})}, \tag{A18}$$

and

$$\sum_i \int dt'[\partial_t\mathcal{G}^{(i)}(t-t')]^2=\sum_{\alpha}\int dt'[\partial_t\mathcal{G}^{(\alpha)}(t-t')]^2 =\sum_{\alpha}\frac{k_BT}{I}=3\frac{k_BT}{I}. \tag{A19}$$

Therefore

$$\sum_i B_i=2\gamma_1^{\mathrm{iso}}k_BT\sum_{\alpha}\int dt'[\mathcal{G}^{(\alpha)}(t-t')]^2=\sum_{\alpha}\frac{k_BT}{\beta+\lambda^{(\alpha)}} \tag{A20}$$

and

$$\sum_i D^i=2\gamma_1^{\mathrm{iso}}k_BT\sum_{\alpha}\int dt'[\partial_t\mathcal{G}^{(\alpha)}(t-t')]^2=\sum_{\alpha}\frac{k_BT}{I} =\frac{3k_BT}{I}. \tag{A21}$$

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