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Anisotropy and nonequilibrium effects on the light scattered from suspension in a nematic solvent

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We investigate the effects produced on the light scattering spectrum by the anisotropic diffusion of impurities in an incompressible nematic solvent. The spectrum is calculated by using a fluctuating hydrodynamic description when the system is both in a fully thermodynamic equilibrium state and in a nonequilibrium steady state induced by a dye-concentration gradient. In the former state, the isotropic pretransitional phase as well as the nematic phase of the solvent are considered. This spectrum is symmetric (Lorentzian) with respect to the frequency shifts, but anisotropic through its explicit dependence on the ratio of the diffusion coefficients of the dye parallel and normal to the mean molecular axis of the nematic. The values of these coefficients were taken from experimental measurements of diffusion of methylred and nitrosodimethylaniline in a *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) solvent. This anisotropy changes the height and the width at mid height with respect to the isotropic case in amounts which for MBBA vary up to 36% and 26%. We also calculate the spectrum in the presence of a concentration gradient of the dye and find that its presence gives rise to an asymmetry of the spectrum in its dependence on the frequency shift; its maximum increases and is displaced with respect to its equilibrium position. The size and direction of this shift are proportional to the magnitude of the dye-concentration gradient and depend on its relative orientation with respect to the scattering vector. For small dimensionless concentration gradients ($\sim 10^{-2}$), this effect is maximum when these vectors are parallel and the scattering angle is low ($\sim 1°$). The maximum degree of departure from equilibrium is significant and turns out to be approximately 55%. In view of the significant changes in the spectrum, our theoretical analysis suggests that these effects might be observable.

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I. INTRODUCTION

In a liquid, fluctuations occur spontaneously and continuously, and the local perturbations arising from them disturb the equilibrium state of the system. As a result, relaxation processes involving a large number of particles are generated, and these slow, collective modes relax toward their equilibrium values. The response of the system can be described in terms of incremental variables and the equations governing them. Since these fluctuations around their average equilibrium value are usually small, the equations describing their space and time variations can be obtained by linearizing the general equations of motion.

The investigation of the effects of fluctuations about nonequilibrium stationary states of simple fluids has attracted increasing attention during the last two decades. Simple fluids subject to a static temperature or pressure gradient have been investigated [1–4], and some of the predicted results were detected by light scattering experiments [5,6]. Similar studies have also been developed for some nonequilibrium stationary states of nematic liquid crystals, such as those generated by a static temperature gradient [7], a stationary shear flow [8], or an externally imposed constant pressure gradient [9,10]. Although in the first two cases it was found that the nonequilibrium contributions to the corresponding light scattering spectra were small, in the case of a Poiseuille flow induced by an external pressure gradient the effect may be quite large and might be observable. However, to our knowledge, at present there is no experimental confirmation of these effects, in spite of the fact that for nematics the scattered intensity is several orders of magnitude larger than for ordinary fluids.

On the other hand, in the last two decades mass diffusion in mesophases has been extensively studied by a variety of experimental methods. Diffusion coefficients have been measured by mass transport and densitometric techniques, by means of NMR spin-echo techniques, and by quasielastic neutron scattering, and detected optically or by radiotracers [11]. Early measurements of mass diffusion in liquid crystals using impurity diffusion have shown that the diffusion is anisotropic in most cases [12,13]. The diffusion of small particles dissolved in nematics (impurity diffusion) has shown that diffusion parallel to the director $(D_{\parallel})$ is faster than perpendicular $(D_{\perp})$ to it. The ratio of these diffusion coefficients seems to be independent of the actual shape of the diffusing molecule [14–16]. However, to our knowledge, investigation of the effects of this asymmetry on the light scattering spectrum has not been considered.

In this paper, we report theoretical results describing the effects on the light scattering spectrum produced by the anisotropic diffusion of impurities in an incompressible nematic solvent. This spectrum is calculated by using a fluctuating hydrodynamic description when the solvent is in both a fully thermodynamic equilibrium state and a nonequilibrium steady state induced by a dye-concentration gradient. We find

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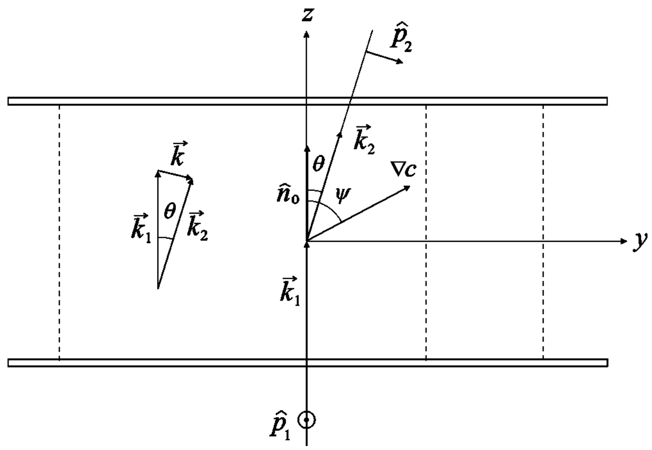

FIG. 1. Schematic representation of a plane homeotropic nematic cell with a concentration gradient in the direction defined by ψ. θ is the scattering angle.

that the height of the central peak in the equilibrium Lorentzian due to transverse director fluctuations is changed and that its shape becomes asymmetric due to the applied concentration gradient by an amount determined by its magnitude. The maximum difference between the nonequilibrium and equilibrium contributions to the spectrum for various values of the external gradient is estimated. It is found that this anisotropy increases with the magnitude of the gradient and has an important effect on the nonequilibrium part of the spectrum. Our theoretical analysis suggests that these effects might be observable.

II. MODEL AND BASIC EQUATIONS

Consider a dilute suspension of noninteracting impurities diffusing through an initially quiescent thermotropic nematic liquid crystal solvent, as depicted in Fig. 1. In nematics, as in ordinary isotropic liquids, sound waves may propagate and all the remaining hydro-dynamic modes are diffusive. In studying the latter, we shall assume that the temperature perturbations are sufficiently small so that the nematic fluid may be regarded as incompressible. There are different forms for introducing this restriction into the set of nematodynamic equations [17,18]. Here we follow the Leslie-Ericksen approach and eliminate the term div$\,\vec{v}$ by setting $\nu_2=\nu_4$ and $\nu_5=0$ [17], where, as we shall define later on, ν_2, ν_4, and ν_5 denote several nematic viscosity coefficients. $\vec{v}(\vec{r},t)$ stands for the nematic's hydrodynamic velocity field.

For the homeotropic configuration in Fig. 1, the chosen initial director's orientation $\hat{n}_0$ is indicated with respect to the origin at the center of the cell so that $\hat{n}_0=(0,0,1)$, and the light scattering process is also sketched. The incident wave vector $\vec{k}_1$ is directed along the z axis, while the scattered wave vector $\vec{k}_2$ is chosen to be in the (scattering) y-z plane. $\hat{p}_1=(1,0,0)$ and $\hat{p}_2=(0,-\cos\theta,\sin\theta)$ denote, respectively, the incident and scattered unit polarization vectors, where θ is the scattering angle. The scattering process is associated with a wave vector change $\vec{k}=\vec{k}_1-\vec{k}_2$ and with a frequency shift $\omega=\omega_1-\omega_2$. It should be pointed out that this scattering geometry is experimentally feasible and corresponds to one of the configurations used by Chatelain [19].We shall analyze only those nonequilibrium states of the suspension for a solvent at rest, defined by the stationary concentration field of impurities

$$c^s(\vec{r}) = c_0 + \vec{r}\cdot\vec{\nabla}c, \tag{1}$$

where $\vec{\nabla}c$ is a uniform concentration gradient on the y-z plane whose direction is specified by the angle ψ in Fig. 1, and c_0 is the impurity concentration at equilibrium. With respect to $\hat{n}_0$ and the wave vector $\vec{k}$ defined above [20], the hydrodynamic variables of the nematic solvent may be divided into two independent sets, namely, transverse and longitudinal. The former set is $\{n_x(\vec{r},t),v_x(\vec{r},t)\}$, while the latter is $\{\rho(\vec{r},t),\sigma(\vec{r},t),v_y(\vec{r},t),v_z(\vec{r},t),n_y(\vec{r},t)\}$. Here $\rho(\vec{r},t)$ and $\sigma(\vec{r},t)$ are, respectively, the local mass density and the volume density entropy. The specific entropy (entropy per unit mass) $s(\vec{r},t)$ is related to $\sigma(\vec{r},t)$ through $s=\sigma\rho^{-1}$, and $\hat{n}(\vec{r},t)$ is the unitary director field.

The hydrodynamic description of a uniaxial nematic liquid crystal is well established and has been verified experimentally in detail [21–24]. Its generalization to include electrohydrodynamic effects has also been accomplished, triggered by the many electro-optic effects existing in these liquids which have produced a variety of applications in display devices [25]. If the suspension is sufficiently diluted, the presence of the impurities does not appreciably perturb the dynamics of the liquid crystal, and linear deviations around an equilibrium state defined by ρ_0, n_i^0, and s_0 will be denoted by $\delta\rho(\vec{r},t)=\rho(\vec{r},t)-\rho_0$, $\delta v_i(\vec{r},t)=v_i(\vec{r},t)$, $\delta n_i(\vec{r},t)=n_i(\vec{r},t)-n_i^0$, and $\delta s(\vec{r},t)=s(\vec{r},t)-s_0$. The description of the hydrodynamic state of the nematic may also be accomplished by using the pressure field $p(\vec{r},t)$ instead of the density field $\rho(\vec{r},t)$, or the temperature field $T(\vec{r},t)$ instead of the entropy field $\sigma(\vec{r},t)$, since these fluctuations are related through well known thermodynamic relations [26].

Years ago Landau and Lifshitz [27] proposed a pioneering method to describe fluctuations about equilibrium states where the fluctuation-dissipation theorem and linear response can be used effectively. Their justification in terms of the general framework of Onsager's theory of irreversible processes [28,29] was achieved by Fox and Uhlenbeck [28–31], and their formulation allowed for the use of state variables which did not posses a definite time reversal symmetry. This generalization is necessary for applications to the hydrodynamics of simple and complex fluids such as liquid crystals. The equations of motion for the above thermal fluctuations are derived from the well known general hydrodynamic equations for a nematic [17,18,32,33] by introducing fluctuating components into the momentum current of the solvent, $\sigma_{ij}(\vec{r},t)$, the entropy current $j_i^s(\vec{r},t)$, and the relaxation quasicurrent of the orientation of the nematic, Y_i. These stochastic components are, respectively, $\vec{\nabla}_j\Sigma_{ij}(\vec{r},t)$, $J_i^s(\vec{r},t)$, and $\Upsilon_i(\vec{r},t)$ and are chosen so that they are zero averaged stochastic processes $\langle\Sigma_{ij}(\vec{r},t)\rangle=\langle\Upsilon_i(\vec{r},t)\rangle=\langle J_i^s(\vec{r},t)\rangle=0$, satisfying fluctuation-dissipation relations of the form

$$\langle \textstyle\sum_{ij}(\vec{r},t)\sum_{kl}(\vec{r}\,',t')\rangle = 2k_B T_0 \nu^0_{ijkl}\delta(\vec{r}-\vec{r}\,')\,\delta(t-t'), \tag{2}$$

$$\langle \Upsilon_i(\vec{r},t)\Upsilon_j(\vec{r}\,',t')\rangle = 2k_B T_0 \frac{1}{\gamma_1}\delta^{0\perp}_{ij}\,\delta(\vec{r}-\vec{r}\,')\,\delta(t-t'), \tag{3}$$

$$\langle J^\sigma_i(\vec{r},t)J^\sigma_j(\vec{r}\,',t')\rangle = 2k_B\kappa^0_{ij}\delta(\vec{r}-\vec{r}\,')\,\delta(t-t'), \tag{4}$$

where k_B is Boltzmann's constant, γ_1 is a reorientational viscosity of the nematic, and the superscript 0 denotes the linearized quantity. The linearized projection operator $\delta^{0\perp}_{ij}$ and the thermal conductivity tensor κ^0_{ij}, are defined, respectively, by $\delta^{\perp 0}_{ij}=\delta_{ij}-n^0_i n^0_j$ and $\kappa^0_{ij}=\kappa_\perp\delta_{ij}+\kappa_a n^0_i n^0_j$, where δ_{ij} is the usual Kronecker delta, $\kappa_a\equiv\kappa_\parallel-\kappa_\perp$ is the anisotropy in the thermal conductivity, and $\kappa_\perp$ and $\kappa_\parallel$ denote, respectively, its perpendicular and parallel components with respect to the director field. Also, the linearized viscous tensor ν^0_{ijkl} is

$$\begin{aligned}\nu^0_{ijkl} = {}& \nu_2(\delta_{jl}\delta_{ik+}\delta_{il}\delta_{jk}) + 2(\nu_1+\nu_2-2\nu_3)n^0_i n^0_j n^0_k n^0_l \\ & + (\nu_3-\nu_2)(n^0_j n^0_l\,\delta_{ik} + n^0_j n^0_k\delta_{il} + n^0_i n^0_k\delta_{jl} + n^0_i n^0_l\,\delta_{jk}) \\ & + (\nu_4-\nu_2)\,\delta_{ij}\delta_{kl} + (\nu_5-\nu_4+\nu_2)(\delta_{ij}n^0_k n^0_l + \delta_{kl}n^0_i n^0_j).\end{aligned} \tag{5}$$

Here $\nu_i, i=1,\ldots,5$, denote several nematic viscosity coefficients.

This process yields a complete set of linearized hydrodynamic equations for an incompressible nematic in the geometry under consideration. However, as will be shown below, in this case it is unnecessary to know their explicit form. They may be found in Refs. [9] and [26].

Let us now turn our attention to the suspended impurities. If no chemical reactions occur between them, their total number is conserved and their local concentration density $c(\vec{r},t)$ obeys the conservation equation

$$\frac{\delta c}{\delta t} + \vec{\nabla}_i J_i = 0, \tag{6}$$

where $J_i(\vec{r},t)$ is the flux of the diffusing particles, which for a uniaxial nematic is

$$J_i(\vec{r},t) = -D_{ij}(\vec{r},t)\vec{\nabla}_j c(\vec{r},t) + c(\vec{r},t)v_i(\vec{r},t), \tag{7}$$

where $v_i(\vec{r},t)$ is the velocity field of the solvent and $D_{ij}(\vec{r},t)$ is the diffusion tensor of the suspended impurities. For a nematic D_{ij} has the standard uniaxial form

$$D_{ij}(\vec{r},t) = D_\perp\delta_{ij} + D_a n_i(\vec{r},t)n_j(\vec{r},t). \tag{8}$$

Here the diffusion anisotropy is defined as $D_a\equiv D_\parallel - D_\perp$. Using these equations we arrive at the following diffusion equation for $c(\vec{r},t)$:

$$\begin{aligned}\frac{\partial c}{\partial t} = {}& D_\perp\vec{\nabla}^2 c + D_a n_i n_j\vec{\nabla}_i\vec{\nabla}_j c + D_a(n_i\vec{\nabla}_i n_j + n_j\vec{\nabla}_i n_i)\vec{\nabla}_j c \\ & - v_i\vec{\nabla}_i c.\end{aligned} \tag{9}$$

Note that there is an explicit (nonlinear) coupling with the nematic through the dynamics of its direction $n_i(\vec{r},t)$ and velocity fields $v_i(\vec{r},t)$.

To describe the response of the system to small perturbations originating in spontaneous thermal fluctuations, we introduce the incremental variable $\delta c(\vec{r},t)\equiv c(\vec{r},t)-c^s(\vec{r})$ defined with respect to the stationary state $c^s(\vec{r})$. As mentioned above, we shall analyze only those nonequilibrium states of the form (1), which for future use it will be convenient to recast in the equivalent form

$$c^s(\vec{r}) = c_0 + \tilde{a}\sin(\vec{q}\cdot\vec{r}) \tag{10}$$

with

$$\vec{q} \equiv \frac{1}{\tilde{a}}\vec{\nabla}c, \tag{11}$$

provided that we take the limit $q\to 0$. Both $\vec{q}$ and $\tilde{a}$ are auxiliary variables which are introduced in order to simplify the analysis of Eq. (9).

Following Landau and Lifshitz [27], we also introduce a fluctuating mass diffusion current $J^F_i(\vec{r},t)$ into Eq. (7). This quantity is also a Markovian, Gaussian, stochastic process with zero mean $\langle J^F_i(\vec{r},t)\rangle=0$ and a fluctuation-dissipation relation of the form

$$\begin{aligned}\langle J^F_i(\vec{r},t)J^F_j(\vec{r}\,',t')\rangle &= 2D_{ij}c_s(\vec{r})\,\delta(\vec{r}-\vec{r}\,')\,\delta(t-t') \\ &= 2D_{ij}(c_0+\vec{r}\cdot\vec{\nabla}c)\,\delta(\vec{r}-\vec{r}\,')\,\delta(t-t'),\end{aligned} \tag{12}$$

where we have used Eq. (1). The fluctuating linearized equation associated with Eq. (9) then reads

$$\begin{aligned}\frac{\partial\delta c}{\partial t} = {}& (D_\perp\vec{\nabla}^2_\perp + D_\parallel\vec{\nabla}^2_z)\,\delta c + \vec{\nabla}_l c\,\delta v_l + D_a(\vec{\nabla}_l c\vec{\nabla}_z\delta n_l \\ & + \vec{\nabla}_z c\vec{\nabla}_l\delta n_l) - \vec{\nabla}_i J^F_i.\end{aligned} \tag{13}$$

Note that it is coupled with the dynamics of the fluctuations δn_i and δv_i of the solvent.

To carry on the analysis it will be convenient to write the dynamic equations for the solute in Fourier space. To this end we define the Fourier transform of an arbitrary field $\vec{A}(\vec{r},t)$ as

$$\tilde{A}_j(\vec{k},\omega) \equiv \int\!\!\int dt\, d^3r\, A_j(\vec{r},t)\exp\{-i(\vec{k}\cdot\vec{r}-\omega t)\}, \tag{14}$$

where we use a tilde to denote the Fourier transformed quantity. Then, Eq. (13) reads

$$\begin{aligned}\delta\tilde{c}(\vec{k},\omega) = {}& \tilde{G}(\vec{k},\omega)(\vec{\nabla}_l c\,\delta\tilde{v}_l + iD_a k_z\vec{\nabla}_l c\,\delta\tilde{n}_l + iD_a\vec{\nabla}_z c k_l\delta\tilde{n}_l \\ & - ik_l\tilde{J}^F_l),\end{aligned} \tag{15}$$

where the propagator $\tilde{G}(\vec{k},\omega)$ is

$$\tilde{G}(\vec{k},\omega) \equiv (-i\omega + D_\perp k^2_\perp + D_\parallel k^2_z)^{-1}, \tag{16}$$

and the fluctuation-dissipation theorem (12) is now

$$\langle \tilde{J}_l^F(\vec{k},\omega)\tilde{J}_m^F(\vec{k}',\omega')\rangle = 2(2\pi)^4 D_{lm}\delta(\omega+\omega')\Big\{ c_0\delta(\vec{k}+\vec{k}') + \frac{\tilde{a}}{2i}[\delta(\vec{k}+\vec{k}'-\vec{q}) - \delta(\vec{k}+\vec{k}'+\vec{q})]\Big\}, \tag{17}$$

where we have made use of Eq. (10). Also note that $\tilde{G}(\vec{k},\omega)$ satisfies the relation

$$\tilde{G}(-\vec{k},-\omega) = \tilde{G}^*(\vec{k},\omega), \tag{18}$$

where the asterisk denotes complex conjugate.

III. DYNAMIC STRUCTURE FACTOR

When the external concentration gradient vanishes, the system is in equilibrium, Eq. (15) reduces to

$$\delta\tilde{c}(\vec{k},\omega) = -i\tilde{G}(\vec{k},\omega)k_i\tilde{J}_i^F(\vec{k},\omega), \tag{19}$$

and Eq. (17) becomes

$$\langle \tilde{J}_i^F(\vec{k},\omega)\tilde{J}_j^F(\vec{k}',\omega')\rangle = 2(2\pi)^4 c_0 D_{ij}\delta(\vec{k}+\vec{k}')\delta(\omega+\omega'). \tag{20}$$

From Eqs. (19) and (20) it follows that the equilibrium autocorrelation function of concentration fluctuations of the suspended impurities is then given by

$$\langle \delta\tilde{c}(\vec{k},\omega)\delta\tilde{c}(\vec{k}',\omega')\rangle^{\rm eq} = -2(2\pi)^4 c_0 D_{ij}k_i k_j'\tilde{G}(\vec{k},\omega)\tilde{G}(\vec{k}',\omega')\delta(\vec{k}+\vec{k}')\delta(\omega+\omega'), \tag{21}$$

which vanishes for all $\vec{k}'$ and ω' values except for $\vec{k}'=-\vec{k}$ and $\omega'=-\omega$. In this case we have

$$S^{\rm eq}(\vec{k},\omega) \equiv \langle \delta\tilde{c}(\vec{k},\omega)\delta\tilde{c}(-\vec{k},-\omega)\rangle^{\rm eq} = 2(2\pi)^4\delta^4(0)c_0 D_{ij}k_i k_j|\tilde{G}(\vec{k},\omega)|^2, \tag{22}$$

where $S^{\rm eq}(\vec{k},\omega)$ stands for the dynamic structure factor in equilibrium and $|\tilde{G}(\vec{k},\omega)|^2=\tilde{G}(\vec{k},\omega)\tilde{G}^*(\vec{k},\omega)$. To arrive at Eq. (22) use has been made of the property (18).

Let us now consider a nonequilibrium state where the concentration gradient components $\vec{\nabla}_j c$ are different from zero. Then the concentration fluctuations in Fourier space, $\delta\tilde{c}(\vec{k},\omega)$, of the solute are given by Eq. (15), while the fluctuation-dissipation theorem for the stochastic density current $\tilde{J}_i^F(\vec{k},\omega)$ is given by Eq. (17). Then, the concentration autocorrelation function is obtained from Eq. (15) by first evaluation $\delta\tilde{c}$ at $\vec{k}'=\vec{k}$ and $\omega'=\omega$ and then multiplying by $\delta c(\vec{k},\omega)$ and averaging the result over an equilibrium ensemble. Using the fact that $\tilde{J}_i^F$, $\delta\tilde{v}_i$, and $\delta\tilde{n}_i$ are uncoupled, we arrive at

$$\begin{aligned}\langle \delta\tilde{c}(\vec{k},\omega)\delta\tilde{c}(\vec{k}',\omega')\rangle &= -\tilde{G}(\vec{k},\omega)\tilde{G}(\vec{k}',\omega')\{k_i k_j'\langle \tilde{J}_i^F(\vec{k},\omega)\tilde{J}_j^F(\vec{k}',\omega')\rangle \\ &\quad - \vec{\nabla}_i c\vec{\nabla}_j c\langle \delta\tilde{v}_i(\vec{k},\omega)\delta\tilde{v}_j(\vec{k}',\omega')\rangle \\ &\quad + D_a^2\langle \delta\tilde{n}_i(\vec{k},\omega)\delta\tilde{n}_j(\vec{k}',\omega')\rangle \\ &\quad \times[k_z k_z'\nabla_i c\nabla_j c + k_z k_j'\nabla_z c\nabla_i c + k_z k_i'\nabla_z c\nabla_j c \\ &\quad + k_i k_j'(\nabla_z c)^2]\}.\end{aligned} \tag{23}$$

Note that in contrast to Eq. (21) in the nonequilibrium situation the density gradient introduces a coupling between the concentration fluctuations δc of the solute and the velocity, δv_j, and orientation fluctuations, δn_j. However, from Eq. (23) it is clear that the contribution of such coupling is second order in the density gradient. Therefore, for sufficiently small density gradients these contributions may be neglected compared to the first order contributions contained in the correlation of the noises J_i^F, Eq. (17), through $\tilde{a}$. Thus

$$\begin{aligned}\langle \delta\tilde{c}(\vec{k},\omega)\delta\tilde{c}(\vec{k}',\omega')\rangle &= -2(2\pi)^4 k_l k_m' D_{lm}\tilde{G}(\vec{k},\omega)\tilde{G}(\vec{k}',\omega')\delta(\omega+\omega') \\ &\quad \times\Big\{ c_0\delta(\vec{k}+\vec{k}') + \frac{\tilde{a}}{2i}\Big[\delta(\vec{k}+\vec{k}'-\vec{q}) - \delta(\vec{k}+\vec{k}'+\vec{q})\Big]\Big\} \\ &\equiv \langle \delta c(\vec{k},\omega)\delta c(\vec{k}',\omega')\rangle^{\rm eq} + \langle \delta c(\vec{k},\omega)\delta c(\vec{k}',\omega')\rangle^{\rm neq}.\end{aligned} \tag{24}$$

It is convenient to rewrite the nonequilibrium contribution in the form

$$\langle \delta\tilde{c}(\vec{k},\omega)\delta\tilde{c}(\vec{k}',\omega')\rangle^{\rm neq} = -2(2\pi)^4 k_l k_m' D_{lm}\tilde{G}(\vec{k},\omega)\tilde{G}(\vec{k}',\omega') \times \delta(\omega+\omega')\frac{\tilde{a}}{2i}\sum_{\epsilon=\pm1}\epsilon\delta(\vec{k}+\vec{k}'-\epsilon\vec{q}). \tag{25}$$

Accordingly, if we now substitute

$$\vec{k}\to\vec{k}+\frac{\epsilon\vec{q}}{2}, \quad \vec{k}'\to\vec{k}'+\frac{\epsilon\vec{q}}{2} \tag{26}$$

into the right hand side of Eq. (25), we obtain

$$\begin{aligned}\langle \delta\tilde{c}(\vec{k},\omega)\delta\tilde{c}(\vec{k}',\omega')\rangle^{\rm neq} &= -2(2\pi)^4 D_{ij}\delta(\omega+\omega')\delta(\vec{k}+\vec{k}') \\ &\quad \times\frac{\tilde{a}}{2i}\sum_{\epsilon=\pm1}\Bigg[\epsilon\left(k_i+\frac{\epsilon q_i}{2}\right)\left(k_j'+\frac{\epsilon q_j}{2}\right)\tilde{G}\left(\vec{k}+\frac{\epsilon\vec{q}}{2},\omega\right) \\ &\quad \times\tilde{G}\left(\vec{k}'+\frac{\epsilon\vec{q}}{2},\omega'\right)\Bigg].\end{aligned} \tag{27}$$

Notice that the nonequilibrium contribution to the structure factor is different from zero only for $\vec{k}'=-\vec{k}$ and $\omega'=-\omega$. Then, after explicit evaluation of the summation over the variable ϵ, we arrive at

$$\langle \delta\widetilde{c}(\vec{k},\omega)\,\delta\widetilde{c}(\vec{k}',\omega')\rangle^{\mathrm{neq}} = -\,\widetilde{a}\left(k_i + \frac{q_i}{2}\right) D_{ij}\left(k_j - \frac{q_j}{2}\right) \times \mathrm{Im}\left\{ \widetilde{G}\left(\vec{k}+\frac{\vec{q}}{2},\omega\right)\widetilde{G}^{*}\left(\vec{k}-\frac{\vec{q}}{2},\omega'\right)\right\}, \tag{28}$$

where Im denotes the imaginary part. We also made use of the symmetry of D_{ij} and Eq. (18).

After a direct calculation from the definition of $\widetilde{G}(\vec{k},\omega)$ we obtain

$$\mathrm{Im}\left\{ \widetilde{G}\left(\vec{k}+\frac{\vec{q}}{2},\omega\right)\widetilde{G}^{*}\left(\vec{k}-\frac{\vec{q}}{2},\omega'\right)\right\} = -\,2\omega(D_{\parallel}k_z q_z + D_{\perp}k_{\perp}q_{\perp}) \times \left|\widetilde{G}\left(\vec{k}+\frac{\vec{q}}{2},\omega\right)\right|^{2}\left|\widetilde{G}\left(\vec{k}-\frac{\vec{q}}{2},\omega'\right)\right|^{2}. \tag{29}$$

Replacing Eq. (29) into Eq. (28), taking the limit $q\rightarrow 0$, and using Eq. (22), we arrive at

$$S^{\mathrm{neq}}(\vec{k},\omega) \equiv \langle \delta\widetilde{c}(\vec{k},\omega)\,\delta\widetilde{c}(-\vec{k},-\omega)\rangle^{\mathrm{neq}} = -\,2\langle \delta\widetilde{c}(\vec{k},\omega)\,\delta\widetilde{c}(-\vec{k},-\omega)\rangle^{\mathrm{eq}} \omega\frac{|\vec{\nabla} c|}{c^{0}}(D_{\parallel}k_z \cos\,\psi + D_{\perp}k_{\perp}\,\sin\,\psi)|\widetilde{G}(\vec{k},\omega)|^{2}, \tag{30}$$

where we have introduced explicitly the angle ψ. Thus, the equilibrium plus nonequilibrium contributions to the dynamic structure factor read

$$S(\vec{k},\omega) \equiv S^{\mathrm{eq}}(\vec{k},\omega) + S^{\mathrm{neq}}(\vec{k},\omega) = S^{\mathrm{eq}}(\vec{k},\omega)\left\{1 - 2\omega\frac{|\nabla c|}{c_0}(D_{\parallel}k_z \cos\,\psi + D_{\perp}k_{\perp}\,\sin\,\psi) \times |\widetilde{G}(\vec{k},\omega)|^{2}\right\}. \tag{31}$$

IV. RESULTS

A. Equilibrium

We first calculate the light scattering spectrum of the suspended impurities when there is no concentration gradient present for a solvent both in the nematic phase and in its isotropic phase. To this end, we first take the isotropic limit of the dynamic structure factor in the equilibrium equation (22) by making the substitutions $D_{ij}=D_{\mathrm{iso}}\delta_{ij}$ and $\vec{k}=\vec{k}_{\mathrm{iso}}$, where D_{iso} denotes the diffusion coefficient of the impurities in the solvent above the clearing point, i.e., in the isotropic phase; $\vec{k}_{\mathrm{iso}}$ is the scattering wave vector associated with a process occurring in the isotropic medium with a refractive index n_{iso}. Furthermore, we shall approximate D_{iso} and n_{iso} by the averages $(D_{\parallel}+2D_{\perp})/3$ and $(n_{\parallel}+2n_{\perp})/3$, where $n_{\parallel}$ and $n_{\perp}$ are the refractive indices of the nematic phase. Note that this implies $D_{\parallel}>D_{\mathrm{iso}}>D_{\perp}$. In the isotropic limit Eq. (22) reads

$$S^{\mathrm{eq}}_{\mathrm{iso}}(\vec{k},\omega) = 2(2\pi)^4\delta^4(0)c_0\frac{D_{\mathrm{iso}}k^2_{\mathrm{iso}}}{\omega^2 + (D_{\mathrm{iso}}k^2_{\mathrm{iso}})^2}. \tag{32}$$

Let us now define the dimensionless equilibrium structure factor of the impurities in the nematic phase of the solvent, $S^{\mathrm{eq}}_0(\omega_0)$, by

$$S^{\mathrm{eq}}_0(\omega_0) \equiv \frac{S^{\mathrm{eq}}(\vec{k},\omega)}{S^{\mathrm{eq}}_{\mathrm{iso}}(\vec{k},0)}, \tag{33}$$

where $S^{\mathrm{eq}}(\vec{k},\omega)$ is given by Eq. (22) and where ω_0 is the dimensionless frequency

$$\omega_0 = \frac{\omega}{D_{\mathrm{iso}}k^2_{\mathrm{iso}}}. \tag{34}$$

Inserting Eqs. (22) and (32) into Eq. (33), we have

$$S^{\mathrm{eq}}_0(\omega_0) = \frac{\alpha}{1+\alpha^2\omega_0^2}, \tag{35}$$

where we have introduced the dimensionless coefficient

$$\alpha \equiv \frac{D_{\mathrm{iso}}k^2_{\mathrm{iso}}}{\mathrm{D}_{\parallel}k_z^2 + D_{\perp}k_{\perp}^2}, \tag{36}$$

which depends on the scattering geometry and on the diffusion coefficients of the solvent both in the isotropic (pretransitional phase) and in the nematic phase. In this sense, α is a parameter that measures the effect of the nematic ordering on the light scattered by the impurities. Since in the isotropic limit $D_{\parallel}=D_{\perp}=D_{\mathrm{iso}}$ and $k=k_{\mathrm{iso}}$, we have that $\alpha=1$ and $S^{\mathrm{eq}}_0(\omega_0)$ reduces to

$$S^{\mathrm{eq}}_{0,\mathrm{iso}}(\omega_0) = \frac{1}{1+\omega_0^2}. \tag{37}$$

This result coincides with that previously obtained in Ref. [34].

The dynamic structure factor (35) is a symmetric Lorentzian with height α and half width at half height $1/\alpha$. Thus, for $\alpha>1$, $S^{\mathrm{eq}}_0(\omega_0)$ is larger and narrower than $S^{\mathrm{eq}}_{0,\mathrm{iso}}(\omega_0)$, while if $\alpha<1$ the dynamic structure factor in the nematic phase becomes smaller and wider than the corresponding one in the isotropic solvent. To illustrate this effect quantitatively, note that in the isotropic case both the incident and scattered beams propagate in a medium with refraction index n_{iso}. Then, as usual [35],

$$k_{\mathrm{iso}} = 2k_0 n_{\mathrm{iso}}\,\sin\frac{\theta}{2}, \tag{38}$$

where k_0 is the magnitude of the wave vector of the incident beam in vacuum.

On the other hand, when the solvent is in the nematic phase, anisotropic effects appear and light propagation inside the sample strongly depends on the polarization of the beams. According to Fig. 1, the incident beam will propagate as in an isotropic medium with refractive index $n_\perp$ (ordinary refractive index) and

$$\vec{k}_1 = k_0 n_\perp \hat{e}_z, \tag{39}$$

where $\hat{e}_z$ is a unit vector along the z axis.

For the scattered beam, the refractive index is the effective refractive index, which depends on the orientation of the vector $\hat{p}_2$ with respect to the optical axis, and is given by

$$n_{\mathrm{eff}}(\theta) = \frac{n_\parallel n_\perp}{[n_\parallel^2 \cos^2\theta + n_\perp^2 \sin^2\theta]^{1/2}}. \tag{40}$$

Here $n_\parallel$ is the refractive index for a linearly polarized beam along the optical axis, i.e., the extraordinary refractive index. Thus, since $\vec{k}=\vec{k}_1-\vec{k}_2$, from Eqs. (39) and (40) we find

$$\vec{k}_2 = k_0 n_{\mathrm{eff}}(\theta)(\hat{e}_z \cos\theta + \hat{e}_y \sin\theta), \tag{41}$$

$$k_\parallel = k_0[n_\perp - n_{\mathrm{eff}}(\theta)\cos\theta], \tag{42}$$

and

$$k_\perp = -k_0 n_{\mathrm{eff}}(\theta)\sin\theta, \tag{43}$$

$\hat{e}_y$ being a unit vector along the y axis. As a result, α may be rewritten as

$$\alpha = \frac{2}{3}\frac{n_{\mathrm{iso}}^2(1-\cos\theta)(1+2\sigma)}{[n_\perp - n_{\mathrm{eff}}(\theta)\cos\theta]^2 + \sigma n_{\mathrm{eff}}^2(\theta)\sin^2\theta}, \tag{44}$$

with $\sigma \equiv D_\perp/D_\parallel$. For small scattering angles we have $n_{\mathrm{eff}}(\theta) \simeq n_\perp$ and

$$\alpha \cong \frac{(1+2\sigma)}{3\sigma}\left(\frac{n_{\mathrm{iso}}}{n_\perp}\right)^2. \tag{45}$$

Since typical values of σ for thermotropic nematics are $\sigma \simeq 0.5 < 1$ and usually $n_{\mathrm{iso}} > n_\perp$, in this limit we have $\alpha > 1$. For instance, experimental data for the diffusion of two different dyes (methylred and nitrosodimethylaniline) in the thermotropic nematic N-(p-methoxybenzylidene)-p-butylaniline (MBBA) gives for both dyes $\sigma \simeq 0.6$ [14]. Moreover, for MBBA the ordinary and extraordinary refractive indices are, respectively, $n_\perp = 1.56$ and $n_\parallel = 1.81$ [25], so we have $n_{\mathrm{iso}} \simeq 1.64$. In this form we obtain $\alpha \simeq 1.36$ for $\theta = 1°$.

Let us define Δ_h^{eq} as the relative change in the height of the equilibrium spectrum with respect to the isotropic case, that is,

$$\Delta_h^{\mathrm{eq}} \equiv \frac{S_0^{\mathrm{eq}}(0) - S_{0,\mathrm{iso}}^{\mathrm{eq}}(0)}{S_{0,\mathrm{iso}}^{\mathrm{eq}}(0)} = \alpha - 1. \tag{46}$$

Similarly, the relative width change at half height, $\Delta_\omega^{\mathrm{eq}}$, is

$$\Delta_\omega^{\mathrm{eq}} \equiv \frac{\omega^{(1/2)} - \omega_{\mathrm{iso}}^{(1/2)}}{\omega_{\mathrm{iso}}^{(1/2)}} = \frac{1}{\alpha} - 1, \tag{47}$$

where $\omega^{(1/2)}$ and $\omega_{\mathrm{iso}}^{(1/2)}$ denote, respectively, the frequency for which the equilibrium spectrum, in the nematic or isotropic phase, has half maximum height. For the particular experimental situation considered above [14], we find $\Delta_h^{\mathrm{eq}} \simeq 0.36$, i.e., a height increment of 36%, and $\Delta_\omega^{\mathrm{eq}} \simeq -0.26$, a width decrease of 26%. These results are plotted in Fig. 2. Note that as the scattering angle increases, a decreases monotonically and eventually it takes values lower than unity. For example, in the particular case of dye diffusion in MBBA discussed above with $\theta = 85°$, we have $\alpha = 0.92$, $\Delta_h^{\mathrm{eq}} \simeq -0.076$, and $\Delta_\omega^{\mathrm{eq}} \simeq 0.082$. This behavior is illustrated in the inset of Fig. 2.

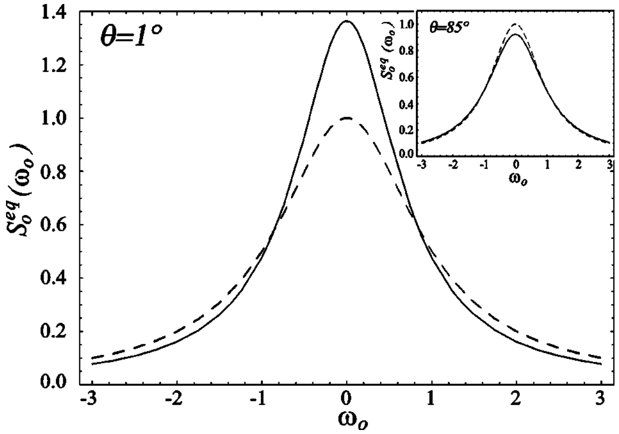

FIG. 2. Normalized structure factor $S_0^{\mathrm{eq}}(\omega_0)$ as defined by Eq. (35), plotted vs normalized frequency ω_o. (—) corresponds to the nematic phase and (– – –) represents the isotropic contribution, α is calculated from Eq. (45) for the values of the material parameters given in Sec. IV and for a small ($\theta = 1°$) and a large ($\theta = 85°$) value of θ.

B. External concentration gradient

We shall now analyze the effect of the impurity concentration gradient on the dynamic structure factor, restricting ourselves to considering a solvent in the nematic phase. Following the same procedure, we define a normalized dynamic structure factor $S_0(\omega_0)$ which contains both the equilibrium and nonequilibrium contributions,

$$\begin{aligned} S_0(\omega_0) &\equiv \frac{S(\vec{k},\omega)}{S_{\mathrm{iso}}^{\mathrm{eq}}(\vec{k},0)} \\ &= S_0^{\mathrm{eq}}(\omega_0)\left\{1 + 2\frac{|\vec{\nabla}c|}{c_0}\frac{k_z\cos\psi + \sigma k_\perp \sin\psi}{k_z^2 + \sigma k_\perp^2} \right. \\ &\qquad \left. \times \frac{\alpha\omega_0}{1+\alpha^2\omega_0^2}\right\}, \end{aligned} \tag{48}$$

where $S(\vec{k},\omega)$ and $S_{\mathrm{iso}}^{\mathrm{eq}}(\vec{k},0)$ are defined by Eqs. (31) and (32), respectively. By using Eqs. (42) and (43), Eq. (48) may be rewritten as

$$S_0(\omega_0) = S_0^{\mathrm{eq}}(\omega_0) + S^{\mathrm{neq}}(\omega_0) = S_0^{\mathrm{eq}}(\omega_0)\left\{1 + 2\gamma_c\beta\frac{\alpha\omega_0}{1+\alpha^2\omega_0^2}\right\}, \tag{49}$$

where γ_c is the dimensionless concentration gradient

$$\gamma_c \equiv \frac{|\vec{\nabla} c|}{k_0 c_0}, \tag{50}$$

and

$$\beta = \beta(\theta,\psi;\sigma) \equiv \frac{[n_\perp - n_{\text{eff}}(\theta)\cos\,\theta]\cos\,\psi - \sigma n_{\text{eff}}(\theta)\sin\,\theta\,\sin\,\psi}{[n_\perp - n_{\text{eff}}(\theta)\cos\,\theta]^2 + \sigma n_{\text{eff}}^2(\theta)\sin^2\,\theta} \tag{51}$$

is a dimensionless function that quantifies the effect of the relative orientation of the density gradient and the scattering vector. Notice that, in the isotropic limit $n_\perp = n_\parallel = n_{\text{iso}}$ and $\sigma = 1$, β reduces to

$$\beta_{\text{iso}} = \frac{\sin(\theta/2 - \psi)}{2 n_{\text{iso}} \sin^2(\theta/2)}, \tag{52}$$

while for small scattering angles, $\sin\,\theta \cong \theta, \cos\,\theta \cong 1$,

$$\beta \cong -\frac{\sin\,\psi}{\theta n_\perp}, \quad \theta \ll 1, \tag{53}$$

where use has been made of the fact that $n_{\text{eff}}(\theta) \simeq n_\perp$ for small θ. Therefore, in this limit the nonequilibrium contribution to the dynamic structure factor may be important due to the dependence of β on θ^{-1}. In the following we will restrict ourselves to the case where $\theta \ll 1$, for instance, $\theta \simeq 1°$, but ψ will remain unrestricted. Equation (53) also shows that for small scattering angles the largest nonequilibrium effect is obtained for the value $\psi = \pi/2$, that is, when the incident light beam and the external gradient are perpendicular, or, equivalently, when the scattering vector and the density gradient are parallel. This fact is qualitatively similar to the experimental observations of the effects induced by a temperature gradient on the light scattering spectrum of liquid water performed by Beysens *et al.* [5]. Note that γ_c may take only small values $|\gamma_c| \ll 1$ which are compatible with linear irreversible thermodynamics, for instance, $\gamma_c \simeq 10^{-2}$.

From Eq. (49) it is clear that the density gradient introduces an asymmetry in the spectrum which consists in an increment and a displacement of its maximum with respect to its equilibrium position. In order to calculate the magnitude of the frequency shift $\tilde{\omega}_0$ as function of γ_c, we take the derivative of Eq. (49) with respect to ω_0 and equate the result to zero. This yields the condition

$$\alpha^3 \tilde{\omega}_0^3 + 3\gamma_c \beta \alpha^2 \tilde{\omega}_0^2 + \alpha \tilde{\omega}_0 - \gamma_c \beta = 0. \tag{54}$$

Expanding $\tilde{\omega}_0$ in a power series of γ_c we have, up to first order in γ_c,

$$\tilde{\omega}_0 = \frac{\beta}{\alpha} \gamma_c. \tag{55}$$

Therefore, the maximum is shifted by an amount proportional to the density gradient.

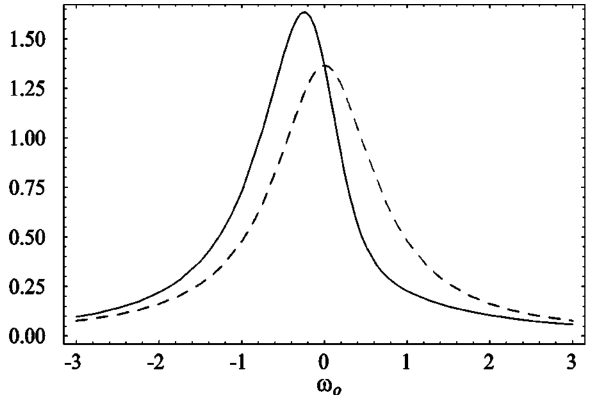

FIG. 3. Normalized structure factor $S_0(\omega_0)$ as given by Eq. (49) vs normalized frequency ω_0 for $\theta \sim 1°$, $\psi = \pi/2$, and β calculated from Eq. (53) with $n_\perp = 1.56$. (—) corresponds to $\gamma_c = 1.5 \times 10^{-2}$ and (– – –) to $\gamma_c = 0$.

The relative difference between the structure factor (49) and the equilibrium structure factor (35) as a function of the frequency ω_0 may be quantified by introducing the following function:

$$\Delta_1^{\text{neq}}(\omega_0) \equiv \left| \frac{S_0(\omega_0) - S_0^{\text{eq}}(\omega_0)}{S_0^{\text{eq}}(\omega_0)} \right| = \left| 2\gamma_c \beta \frac{\alpha \omega_0}{1 + \alpha^2 \omega_0^2} \right|, \tag{56}$$

which has a maximum at the frequency $\hat{\omega}_0 = \pm(\alpha)^{-1}$. In other words, the largest relative difference between $S_0(\omega_0)$ and $S_0^{\text{eq}}(\omega_0)$ due to γ_c is obtained at $\hat{\omega}_0$ and turns out to be

$$\Delta_1^{\text{neq}}(\hat{\omega}_0) = |\gamma_c \beta|. \tag{57}$$

These effects of the solute concentration gradient on its dynamic structure factor may be illustrated by considering again the experimental value $\sigma \simeq 0.6$, corresponding to the diffusion of dye impurities in nematic MBBA, $n_\parallel = 1.81$, $n_{\text{iso}} \simeq 1.64$, and $\theta = 1°$. In Fig. 3 we plot and compare both $S_0(\omega_0)$ and $S_0^{\text{eq}}(\omega_0)$ by taking $\psi = \pi/2$ for $\gamma_c = 1.5 \times 10^{-2}$. We obtain a frequency shift $\tilde{\omega}_0 = -0.40$ and a maximum relative change of the spectrum $\Delta_1^{\text{neq}} \simeq 0.55(55\%)$ at $\hat{\omega}_0 = \pm 0.73$.

V. CONCLUDING REMARKS

Summarizing, by using a fluctuating hydrodynamic approach we have investigated theoretically the influence of the effects produced by a uniform impurity concentration gradient on the light scattering spectrum of a suspension in a nematic solvent. We considered both the isotropic pretransitional as well as the nematic phase of the solvent, when the system is in a fully thermodynamic equilibrium state and in a nonequilibrium steady state induced by a dye-concentration gradient. In the former state, the spectrum is symmetric (Lorentzian) with respect to the frequency shifts, but anisotropic through its explicit dependence on the ratio of the diffusion coefficients of the dye, parallel and normal to the mean molecular axis of the nematic. The values of these coefficients were taken from experimental measurements on the diffusion of methylred and nitrosodimethylaniline in a

MBBA solvent. Our results showed that the anisotropy increases the height and decreases the width at midheight with respect to the isotropic case in amounts which vary up to 36% and 26% for MBBA.

It should be emphasized again that the nonequilibrium correction is an odd function of ω that introduces an asymmetry in the shape of the structure factor, shifting the maximum toward the region of negative values of ω. Close to equilibrium, the size and direction of this shift are proportional to the magnitude of the dye-concentration gradient and depend on its relative orientation with respect to the initial director's orientation. For small dimensionless concentration gradients $(\sim 10^{-2})$, this effect is maximum when these vectors are perpendicular and the scattering angle is low $(\sim 1°)$ and the size of the shift depends on the magnitude of the gradient, as indicated in Fig. 3.

The k dependences $S_0^{\mathrm{eq}}(\vec{k},\omega) \sim k^{-2}$ and $S^{\mathrm{neq}}(\vec{k},\omega) \sim k^{-3}$ are related to the nature of the variables involved. For a simple fluid all the variables are conserved, whereas for a nematic the orientation state variables are not conserved.

To our knowledge, the physical situation dealt with here has not been considered in the literature and our approach yields results that might be observable.

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