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Microscopic Theory of Flow Alignment in Nematic Liquid Crystals

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A microscopic theory of the flow alignment in nematic liquid crystals is presented. The calculation is based on a thermodynamic sum rule derived earlier. The temperature dependence of the flow-alignment angle is obtained in terms of the nematic order parameter $S(T)$. The theory favors stable flow alignment, but the orientational instability found by Gähwiller cannot be ruled out.

The hydrodynamic theory of nematic liquid crystals[1-3] predicts that under stationary shear flow, the director, or averaged molecular orientation, stabilizes at an angle θ relative to the direction of flow which is given by

$$\cos(2\theta) = -\gamma_1/\gamma_2 = 1/\lambda, \tag{1}$$

where γ_1 and $-\gamma_2$ are usually interpreted as two counteracting viscous torque coefficients. In isotropic molecular liquids there is a weak flow alignment at an angle of 45° relative to the direction of flow.[4] Strong alignment, at an angle $\theta(T)$ which is much smaller than 45° and has a marked temperature dependence, is a phenomenon specific to liquid crystals, and it is therefore of particular interest.

In this Letter I present a simple calculation from first principles of the temperature-dependent flow-alignment angle $\theta(T)$. To my knowledge this is the first microscopic calculation of a hydrodynamic coefficient for nematics. The result reported here agrees with the earlier model calculations by Helfrich[5] at low temperature when the nematic order is perfect and the molecules are assumed to be rigid ellipsoids. The present theory is in good, if qualitative, agreement with recent measurements of $\theta(T)$ by Meiboom and Hewitt[6] which were performed on three nematic substances, PAA (p-azoxyanisole), MBBA {N-[p-methoxybenzylidine]-p-butylaniline}, and HBAB (p-n-hexyloxybenzylidine-p'-aminobenzonitrile). At variance with these experiments are measurements by Gähwiller[7] who reported that for HBAB flow alignment does not occur below 91.8°C. While the present theory does not conclusively rule out this possibility, which amounts to $\lambda < 1$ in Eq. (1), it makes it unlikely.

In the rederivation of nematic hydrodynamics given by Forster *et al.*,[2,3] γ_1^{-1} appears as a rotational relaxation coefficient, as it does in the original Leslie-Ericksen theory. However, my rederivation insists that γ_2 is not an independent dissipative coefficient. Rather, the ratio $\lambda = -\gamma_2/\gamma_1$ enters the theory as an independent reactive coefficient which characterizes the reversible response of the director field to symmetric local stress. One might expect, therefore, that λ can be computed by equilibrium statistical mechanics.

This is true at least for the dominant part of λ.

By means of a time-correlation function analysis,[3] I have shown that the following sum rule holds:

$$\tfrac{1}{2}(\lambda-1)-\tilde{\mu}=\lim_{k\to 0}(1/ik)\int d^3(r-r')e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}\langle[g_3(\vec{r}),n_1(\vec{r}\,')]_{\mathrm{PB}}\rangle, \tag{2}$$

where the limit in $\vec{k}$ is to be taken from the 1 direction, in keeping with the uniaxial nematic symmetry.[8] $g_3(\vec{r})=\vec{n}^0\cdot\vec{g}(\vec{r})$ is the component of the microscopic momentum density parallel to the equilibrium director $\vec{n}^0$, and $n_1(\vec{r})$ is the transverse component of the local microscopic director. The subscript PB indicates a classical Poisson bracket. Equation (2), with $\tilde{\mu}=0$, has also been given by Martin, Parodi, and Pershan.[9] Its analog in a superfluid expresses the superfluid density ρ_s as a commutator involving the mass density ρ and the microscopic superfluid momentum-density operator $\vec{g}_s$. $\tilde{\mu}$ in Eq. (2) is a dynamical contribution. While there is no rigorous argument to suggest that $\tilde{\mu}=0$, or even to predict the sign of $\tilde{\mu}$, I shall argue below that $\tilde{\mu}$ is so small that it can be omitted from Eq. (2).

The remaining, and principal, contribution to λ can be easily calculated. In terms of the symmetric and traceless local order parameter $R_{ij}(\vec{r})$, introduced by de Gennes and Lubensky,[10] n_1 is defined by

$$n_1(\vec{r})\equiv\tfrac{2}{3}R_{13}(\vec{r})/\langle R_{33}(\vec{r})\rangle.$$

We take for R_{ij} the quadrupolar term in the mass density,

$$R_{ij}(\vec{r})=\sum_{\alpha k}m^{\alpha k}[\xi_i^{\alpha k}\xi_i^{\alpha k}-\tfrac{1}{3}\delta_{ij}(\vec{\xi}^{\alpha k})^2]\delta(\vec{r}-\vec{r}^{\,\alpha}), \tag{3}$$

$$\vec{g}(\vec{r})=\sum_{\alpha k}\vec{p}^{\,\alpha k}\delta(\vec{r}-\vec{r}^{\,\alpha k}), \tag{4}$$

where $\vec{r}^{\,\alpha k}$, $\vec{p}^{\,\alpha k}$, and $m^{\alpha k}$ are respectively the coordinate, momentum, and mass of the kth particle in the αth molecule; $\vec{\xi}^{\alpha k}=\vec{r}^{\,\alpha k}-\vec{r}^{\,\alpha}$; and $\vec{r}^{\,\alpha}$ is the molecular center of mass. Omitting only terms of order $\nabla\nabla$, we then easily obtain the Poisson bracket:

$$\begin{aligned}\langle[g_k(\vec{r}),R_{ij}(\vec{r}\,')]_{\mathrm{PB}}\rangle=[\delta_{ki}Q_{jl}+\delta_{kj}Q_{il}-\delta_{kl}Q_{ij}-\tfrac{2}{3}\delta_{ij}Q_{kl}]\nabla_l\delta(\vec{r}-\vec{r}\,')\\+\tfrac{1}{3}Q[\delta_{ki}\delta_{jl}+\delta_{kj}\delta_{il}-\tfrac{2}{3}\delta_{kl}\delta_{ij}]\nabla_l\delta(\vec{r}-\vec{r}\,'),\end{aligned} \tag{5}$$

where

$$\begin{aligned}Q_{ij}&\equiv\langle R_{ij}(\vec{r})\rangle=n(I_l-I_t)S(n_i^0n_j^0-\tfrac{1}{3}\delta_{ij}),\\Q&=n(I_l+2I_t).\end{aligned} \tag{6}$$

Here, $S=\frac{1}{2}\langle 3\cos^2(\theta^\alpha)-1\rangle$ is the conventional dimensionless order parameter, $n=N/V$ is the molecular number density, and $I_l=I_3$ and $2I_t=I_1+I_2$ are given by

$$I_i=\sum_k m^{\alpha k}(\xi_i^{\alpha k})^2. \tag{7}$$

I_i is, essentially, the ith component of the molecular moment of inertia, evaluated in the system of principal molecular axes. Equation (6) contains the well-justified assumption of rigid, though not necessarily symmetric, melocules. The 3 axis is the molecular axis which is preferentially oriented in the nematic phase—presumably the long axis of the molecule.

From these equations, neglecting $\tilde{\mu}$ in Eq. (2), we obtain for the flow-alignment angle[11]

$$\tan^2[\theta(T)]=[\alpha-S(T)]/[\alpha+2S(T)], \tag{8}$$

where $\alpha=(I_l+2I_t)/(I_l-I_t)$ is a molecular constant. All temperature dependence is contained in the orientational order parameter $S(T)$. Equation (8) is my main result.

Even in the absence of quantitative theory of $S(T)$,[12] Eq. (8) agrees in all qualitative aspects with the experiments by Meiboom and Hewitt. In the isotropic phase, $S=0$, and Frenkel's result $\theta=45°$ obtains. In the nematic phase, S is believed to increase from about 0.4 or 0.5 at T_c to values about 0.8. According to Eq. (12), therefore, the flow-alignment angle θ should decrease with decreasing temperature from its maximum at $T=T_c$, reaching a plateau value of $\tan^2\theta\to I_t/I_l$ as $S\to 1$. This is in qualitative agreement with the measurements by Meiboom and Hewitt. For rigid symmetric ellipsoids of length a and width b, $I_t/I_l=(b/a)^2$, which is the result obtained by Helfrich[5] on the basis of rather more formidable, and less convincing, considerations. Qualitatively, since $\alpha_{\mathrm{PAA}}>\alpha_{\mathrm{MBBA}}>\alpha_{\mathrm{HBAB}}$, we expect that $\theta_{\mathrm{PAA}}>\theta_{\mathrm{MBBA}}>\theta_{\mathrm{HBAB}}$ as observed.

In Fig. 1 I have plotted the function, $\cos 2\theta/(3-\cos 2\theta)$, which according to the present theory should equal $S(T)/2\alpha$. The values of $\theta(T)$ are taken from Ref. 6. As the figure indicates, the data are qualitatively consistent with Eq. (8) and the expected T dependence of the order parameter.[12] No quantitative agreement can be claimed, however. From mean-field theory and some experimental evidence,[12] one expects a sharper rise of $S(T)$ with increasing $T_c - T$. Similarly, if reasonable values for l_t/l_l are inserted in Eq. (8), the theory is quantitatively consistent with experiment only if one assumes that even just below T_c, $S(T)$ takes on values near 0.8. Better agreement could be achieved with the conflicting data obtained by Gähwiller[7] for MBBA.

So long as $\tilde{\mu}$ in Eq. (2) can be neglected, the present theory predicts that $\lambda > 1$ for all elongated molecules $(l_t < l_l)$, i.e., stable flow alignment. A molecular expression for $\tilde{\mu}$ can be written down,[3] namely the Kubo-like formula

$$\tilde{\mu} = \lim_{\epsilon \to 0} (1/k_BT) \int_0^\infty dt\, e^{-\epsilon t} \int d^3(r-r') \langle \sigma_{13}(\vec{r}, t) \dot{n}_1(\vec{r}\,', 0) \rangle, \tag{9}$$

where $\sigma_{13}(\vec{r}, t)$ is the microscopic stress tensor. $\tilde{\mu}$ is therefore determined by nonhydrodynamic, rapid, and spatially short-ranged fluctuations, and it should carry little temperature dependence. A crude estimate of $\tilde{\mu}$ can be obtained as follows: The Kubo expressions for the transport coefficients[2,3] ν_3 and $\xi \equiv \gamma_1^{-1}$ are obtained by replacing, in (9), respectively $\dot{n}_1$ by σ_{13} for ν_3, and σ_{13} by $\dot{n}_1$ for γ_1^{-1}. This would lead to the order-of-magnitude expectation that $|\tilde{\mu}| \approx (\nu_3/\gamma_1)^{1/2}$. Note, however, that the time-correlation function in (9) must vanish at $t=0$ becuase of time-reversal symmetry, thus depressing the value of $\tilde{\mu}$. Thus we expect that $|\tilde{\mu}| \ll (\nu_3/\gamma_1)^{1/2}$. For PAA,[2,6] $\nu_3 \approx 0.024$ and $\gamma_1 > 0.05$. Thus, while the case is not clearcut, it is unlikely that $\tilde{\mu}$ contributes significantly to the flow-alignment angle.

Equation (8) suggests, finally, that increasing the chain length of a nematic molecule tends to decrease the flow-alignment angle. It would be interesting to check this prediction on a homologous series of nematic compounds. If Gähwiller's orientational instability occurs at all, it is more likely to be found for the longer members of a homologous series. For HBAB, Gähwiller's findings have recently received additional support in the shear torque measurements of Pieranski and Guyon.[13] By the argument just given, since α is smaller for HBAB that it is for PAA and MBBA, HBAB is indeed the most likely candidate of the three materials to exhibit the instability.

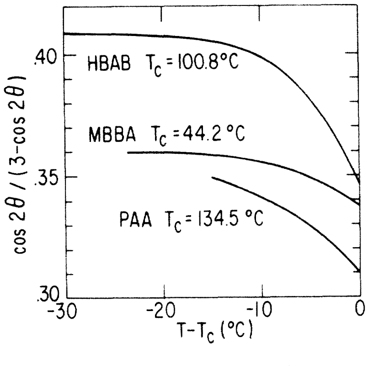

FIG. 1. Flow-alignment angle θ for three nematic liquid crystals as a function of the temperature T. T_c is the clear-point temperature. The ordinate gives $\cos 2\theta/(3-\cos 2\theta)$, predicted to be proportional to the degree of order $S(T)$. Data from Ref. 6.

In a recent Letter, Clark[14] has pointed out that the coefficient λ is continuous across the nematic-isotropic transition. There is no conflict with our result, $3\lambda = 1 + 2\alpha/S$: While we obtain the Frenkel result $\lambda = \infty$ for $T > T_c$, Clark's considerations here apply to the λ which would be measured on a microscopic volume element whose linear dimension is smaller than the correlation length ξ. Near T_c, $\xi \lesssim 200$ Å.

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Temporal Correlations near the Convection-Instability Threshold*

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I analyze Graham's theory of the threshold region of the convection instability in a fluid layer heated from below. I consider the situation where vertical boundary walls insure that a single spatial mode dominates in the threshold region. Equilibrium properties and the temporal correlation times for both the amplitude and intensity of that mode are presented.

In an incisive analysis,[1] Graham has introduced a generalized thermodynamic potential which governs the stability, the dynamics, and the fluctuations in a fluid layer heated from below near the onset of convection. Graham's formulation incorporates both fluctuating forces and the relevant nonlinearities of the hydrodynamic equations to describe the appearance of finite-amplitude convection at the Bénard point. With this theory we can understand the detailed dynamics of fluids for Rayleigh numbers in the immediate neighborhood of the critical Rayleigh number which marks the abrupt appearance of convection in the linear theory.[2] In this note I apply Graham's theory to the experimentally realistic situation of convection in a fluid layer enclosed by rigid vertical walls. I present detailed results on the equilibrium and dynamic behavior of the fluid throughout the convection threshold region.

For experimentally realizable convection cavities, the horizontal dimensions are much smaller than the correlation length of fluctuations near the Bénard point. Thus the rotational and translational symmetry in the fluid plane is effectively broken. To analyze the spatial dependence of the fluid flow one must then calculate the normal modes for the particular geometry of the convection cavity.[3] While the details of such a calculation are indeed complex, the general features are clear. For example, in a rectangular cavity, rolls parallel to the short wall with a wavelength near the critical wavelength (for the infinite-layer problem) suffer the least damping. Thus by properly choosing the dimensions of the experimental cavity, one can insure that *one* normal mode dominates in the threshold region. It is just this one-mode case I investigate.

With the spatial dependence of the convection determined from the normal-mode analysis, only the amplitude, w, of that normal mode remains as a fluctuating quantity. Thus Graham's functional Fokker-Planck equation reduces to an ordinary Fokker-Planck equation[4] for the probability density, $W(w)$, of that one stochastic variable:

$$\frac{\partial W}{\partial t} = -LW = \frac{\partial}{\partial w}\left(\frac{\partial \Phi}{\partial w} W + \frac{\partial W}{\partial w}\right), \tag{1}$$

where $\Phi = w^4/4 - aw^2/2$; w measures the amplitude of the flow in units[5] such that the vertical component of the fluid velocity is $v_z(x,y,z) = wv_0 \times \Psi(x,y,z)$, with $v_0 = (9Q/4rVP^2)^{1/4}(\nu/l)$;

$$a = [a_0]\epsilon = [(9\pi^2/2P)(V/Qr)^{1/2}](R - R_c)/R_c$$

measures the deviation from the critical Rayleigh number; t measures the time in multiples of $[3(V/Qr)^{1/2}(1+P)/P](l^2/\nu)$; $\Psi(x,y,z)$ gives the spatial dependence of the relevant normal mode and is normalized so that $\int \Psi(x,y,z)^2\,dV/V = 1$; and $r = \int \Psi(x,y,z)^4\,dV/V \simeq 2$ is the only quantity which depends on the details of the normal mode (the integrals extend over the entire convection cavity volume, V).

The equilibrium solution to the Fokker-Planck equation is

$$W_0(w) = N\exp(-\Phi) = N\exp(-w^4/4 + aw^2/2), \tag{2}$$

where N normalizes the integral of W_0 over all w to unity. The mean intensity $\langle I\rangle$ ($I = w^2$), the size of its fluctuations, $\langle \Delta I^2\rangle$ ($\Delta I = I - \langle I\rangle$), and the