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Orientational fluctuations in a nematic liquid crystal as seen by neutron scattering

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Real time neutron scattering is used in the study of the slow orientational fluctuations of the director in a nematic sample. A statistical analysis of the observed time series gives the Hurst exponent H and β exponent of the frequency power spectrum that satisfy the scaling relationship $\beta=2H+1$. In the nematic phase, but not in the solid and in the isotropic liquid phases, the exponent values are those expected for a self-organized critical state. When a magnetic field, of the order of the Freedericksz field is applied, the nematic sample is observed to display persistent oscillations of the director. We confront this observation with theoretical predictions.

1. Introduction

The wavelength scale of orientational fluctuations in nematic liquid crystals is limited downwards by the molecular dimension and upwards by the size of the sample container. The long wavelength part is due to fluctuations of the director rather than those of the order parameter. In bulk samples coherent neutron scattering is an ideal tool for studying director fluctuations. These fluctuations are sufficiently slow that they may be studied by a real-time technique, i.e. through the recording of time series of the neutron scattering intensity.

Following de Gennes [1] the orientational fluctuations in a nematic liquid, in zero external field, are in a critical state, independent of temperature. This is thus an example of a self-organized critical system, a term recently introduced by Bak *et al.* [2, 3]. Such systems self-organize to a critical state without tuning of an external parameter, in contrast to the critical state of an equilibrium system which can only be reached through fine-tuning of an external parameter, for example the temperature.

Laboratory experiments on self-organized criticality have so far been performed on macroscopic phenomena, for example avalanches in sandpiles. Other tests of the hypothesis have involved statistical analysis of natural phenomena: earthquakes, river flows, rainfall, etc. A convenient tool for the statistical analysis, also of our director fluctuations, is the rescaled-ranged method (R/S analysis), described by Hurst [4]. The method gives an exponent H, the Hurst exponent. For independent, random processes $H=\frac{1}{2}$. $H\neq\frac{1}{2}$ indicates statistical dependence between past and future events, a characteristic of critical systems [5, 6].

In their pioneering work on orientational fluctuations in nematics de Gennes [7] and coworkers [8] treat only the case of purely relaxational, i.e. aperiodic, non-propagating fluctuations. They do not exclude the existence of propagating modes, however. The present work contains a search for such modes.

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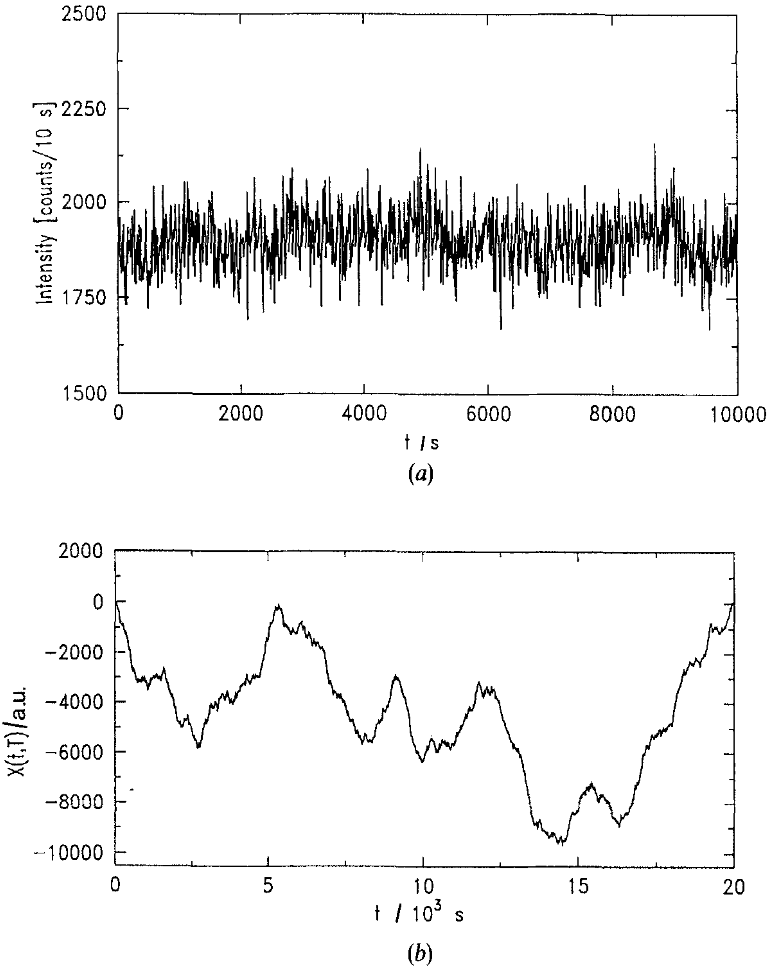

Figure 1. (*a*) Time series of neutron intensity scattered from nematic PAA in zero external field. (*b*) Increment X calculated from (*a*) by means of equation (1) (see text)

2. Experimental

A sample of fully deuterated *para*-azoxyanisole (PAA) is contained in an aluminium vessel of dimensions $(30\times 30\times 3)\,\mathrm{mm}^3$. One of the long dimensions is vertical. A magnetic field, whose strength may be varied, is applied vertically. The mean temperature and the vertical temperature difference across the cell can be varied and controlled within $\sim$0·01°C. PAA is nematic in the temperature range 119–135°C.

The measurements consist of recording the intensity of neutrons scattered from the sample at a wave vector 1·8 $\mathrm{Å}^{-1}$, corresponding to the first coherent liquid diffraction peak. The intensity of this peak depends strongly on the orientation of the director [9], and slow orientational fluctuations of the director are directly observed as temporal fluctuations of the neutron signal. A recorded time series contains up to 2000 points (channels). A typical channel width is 10 s, but shorter or longer widths have also been used. Also the cross-section of the beam can be varied, such as to sample different portions and sizes of the scattering volume.

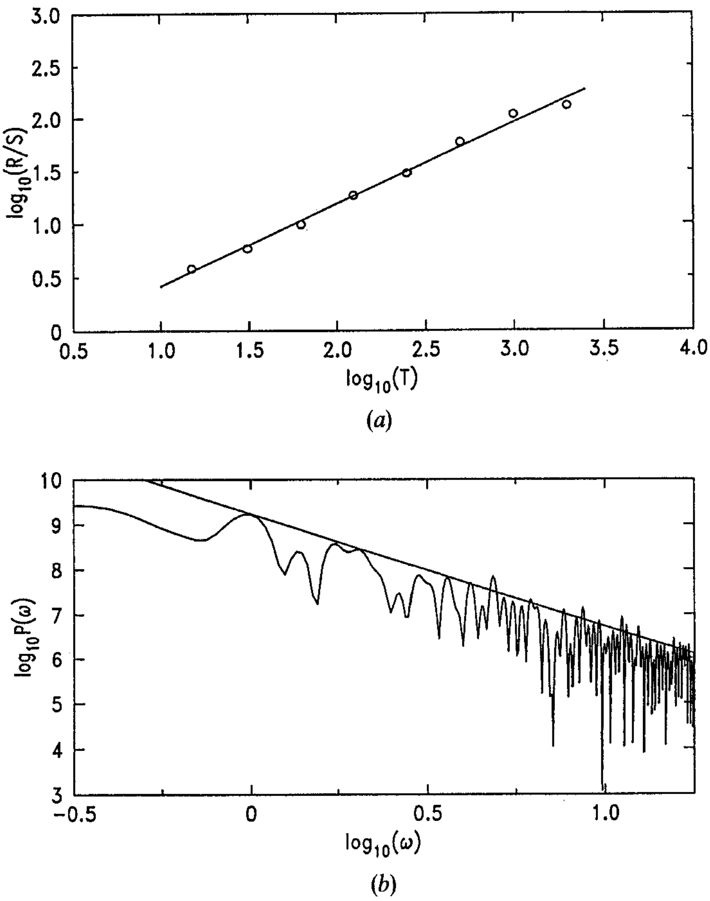

Figure 2. The curve in figure 1 (b) has been used to calculate (a) the Hurst exponent $H=0{\cdot}77$ from the rescaled-range (R/S) method, and (b) the exponent $\beta=2{\cdot}52$ of the power spectrum.

2.1. *Data processing*

A neutron beam of cross section (20 × 20) mm^2 gives the scattering signal used in the R/S analysis. If we denote the recorded time series by $I(t)$, some qualitative information is obtained from the autocorrelation function $c(\tau)=\langle I(t)I(t+\tau)\rangle$. Here τ denotes a time delay. To derive the Hurst exponent, we have to calculate the increment $X(t,T)$, the accumulated departure from the mean intensity [5, 6]

$$X(t,T)=\sum_{u=1}^{t}[I(u)-\langle I\rangle_T], \quad (1)$$

where

$$\langle I\rangle=1/T\sum_{t=1}^{T}I(t), \quad (2)$$

is the average over a time span T. The definitions of R (range) and S (standard deviation) are

$$R(T)=\max X(t,T)-\min X(t,T), \quad (3)$$

for $1\leqslant t\leqslant T$.

$$S(T)=\left\{1/T\sum_{t=1}^{T}[I(t)-\langle I\rangle_T]^2\right\}^{1/2}. \qquad (4)$$

Generally

$$R/S\sim(T/2)^H, \qquad (5)$$

where H denotes the Hurst exponent. The power spectrum $P(\omega)$ of $X(t, T)$ is expected to be of the scaling form

$$P(\omega)\sim\omega^{-\beta}. \qquad (6)$$

A scaling argument [10] gives the following relation

$$\beta=2H+1 \quad \text{with} \quad 0<H<1 \quad \text{and} \quad 1<\beta<3. \qquad (7)$$

An example of the described procedure is given in figures 1 and 2. In figure 1 is shown an observed time series $I(t)$ and the calculated increment $X(t, T)$. From the latter curve we calculate R/S and $P(\omega)$, shown in figure 2, which gives the exponents H and β.

In the subsequent search for oscillatory orientational states in the nematic phase we used a neutron beam 20 mm wide and 3 mm high. A set of raw and processed data is shown in figure 3. The power spectrum, giving the oscillatory frequency, is obtained by a Fourier transform of the auto-correlation function defined above.

2.2. *Experimental results*

Qualitative information about the statistical correlation between fluctuations observed at different times is obtained from the calculation of $C(\tau)$, as alluded to above.

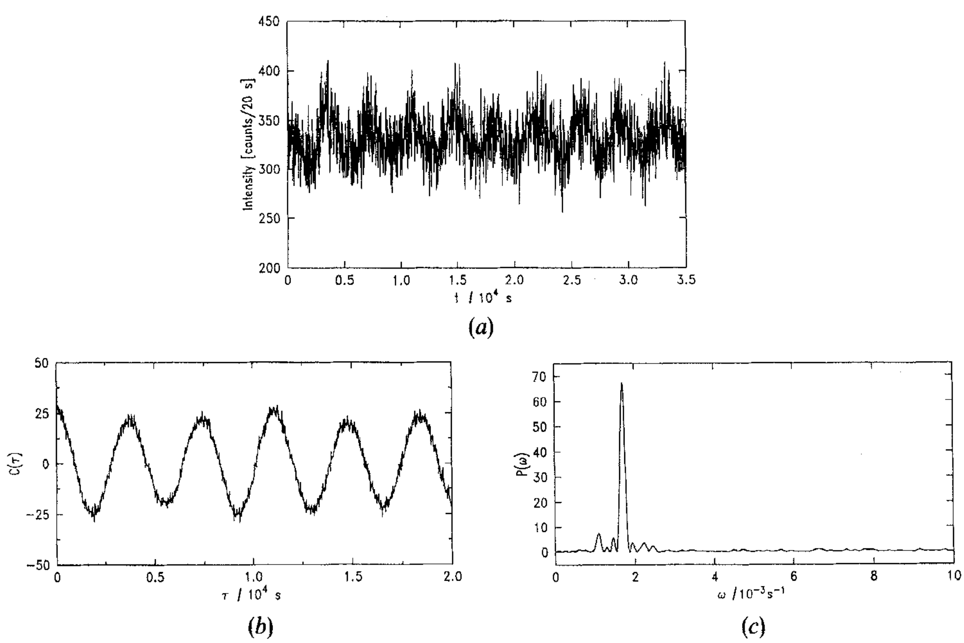

Figure 3. An example of raw and processed data taken at $H=75$ Oe and $\Delta T=-0{\cdot}9°$C (heating from above). (*a*) raw data, (*b*) the autocorrelation function $C(\tau)$, (*c*) the power spectrum.

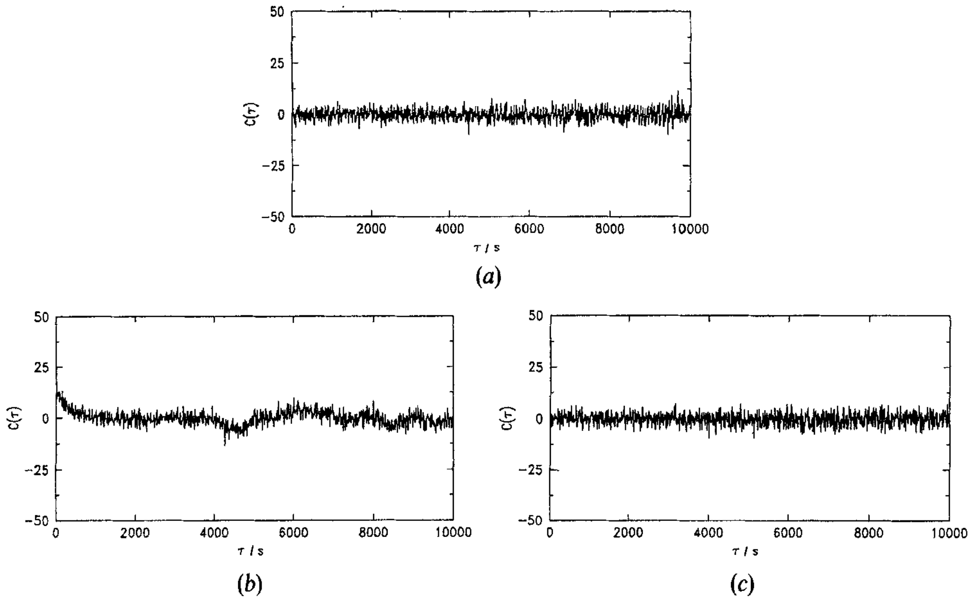

Figure 4. Autocorrelation function $C(\tau)$ obtained in (*a*) solid phase, (*b*) nematic phase, (*c*) isotropic phase.

Experimental values of the exponents H and β for *d*-PAA in its different phases and under different hydrodynamic conditions. The last column is to be compared with β, see equation (7) in the text.

	H	β	$2H+1$
Solid	$0{\cdot}52 \pm 0{\cdot}03$	$2{\cdot}02 \pm 0{\cdot}02$	$2{\cdot}04 \pm 0{\cdot}06$
Nematic			
Quiescent	$0{\cdot}74 \pm 0{\cdot}06$	$2{\cdot}47 \pm 0{\cdot}08$	$2{\cdot}48 \pm 0{\cdot}12$
Convecting	$0{\cdot}74 \pm 0{\cdot}02$	$2{\cdot}42 \pm 0{\cdot}16$	$2{\cdot}48 \pm 0{\cdot}10$
Isotropic	$0{\cdot}56 \pm 0{\cdot}02$	$2{\cdot}10 \pm 0{\cdot}02$	$2{\cdot}12 \pm 0{\cdot}04$

Figure 4 gives examples of $C(\tau)$ observed in three different phases: the solid, the nematic and the isotropic liquid phases. Only the nematic state has the feature expected for statistical correlations. More quantitative information is obtained through the statistical analysis described above, giving the exponents β and H. The table gives a collection of our data [11]. Each number is an averge of exponent values derived from several time series, and the error given is the spread of these values, as measured by the variance. All data were taken without a magnetic field. In the nematic phase data were taken both in the quiescent and in the convecting state obtained when heating from below. In the latter case we made sure to avoid the localized, oscillatory convecting cells reported earlier [12].

In the present search for oscillatory orientational states we applied an adverse temperature gradient, i.e. we heated more from above than from below. Also we applied a vertical magnetic field. The effect of the field on the neutron intensity is seen in

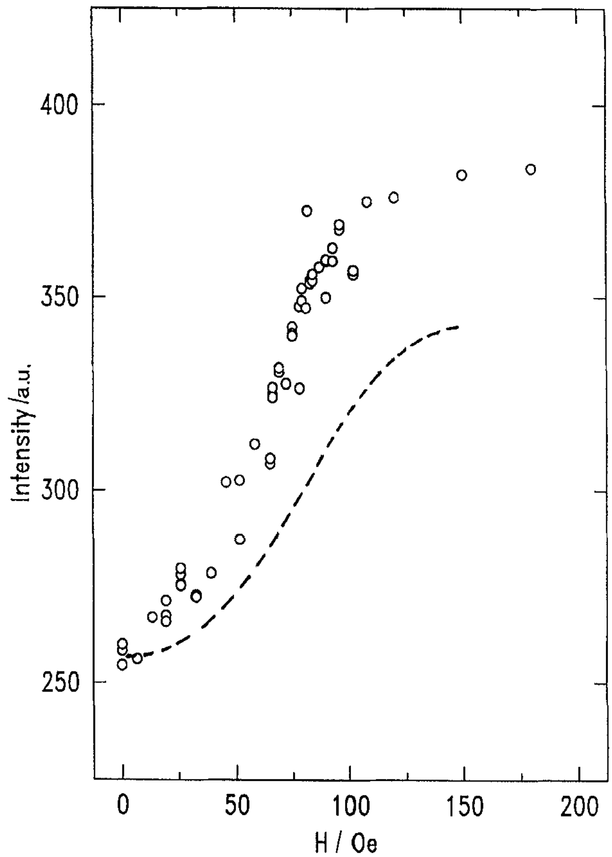

Figure 5. Neutron intensity versus applied, vertical magnetic field at $\Delta T = -0{\cdot}9°C$. The corresponding curve for $\Delta T = -0{\cdot}35°C$ is indicated.

figure 5. No precaution was taken for anchoring the molecules on the walls of the container, and a drawn-out Freedericksz transition is observed. Due to saturation effects we do not expect to be able to observe oscillatory states of fields above 90 Oe.

In the steep part of figure 5 persistent oscillatory states, as exemplified by figure 3, were reproducibly observed, and gave figure 6. At lower fields the observations were erratic and depended on the prehistory, but overall the frequencies were around $1 \times 10^{-3} s^{-1}$. Only at the very lowest fields was the reproducibility sufficiently good such that we have included the data in figure 6.

3. Discussion

The table shows that the Hurst exponent is significantly different from 0·5 only in the nematic phase. This agrees with the expectation alluded to in the Introduction, that a nematic liquid crystal, in zero field, is in a critical state. The data in the isotropic phase were taken 3°C above the clearing point, and are perhaps also subject to some weak orientational fluctuations. The data from the solid phase contain very little physical information and are rather an instrumental check. The density fluctuations existing in the solid phase could only have been observed on a time scale of 10^{-12}, i.e. by conventional inelastic scattering.

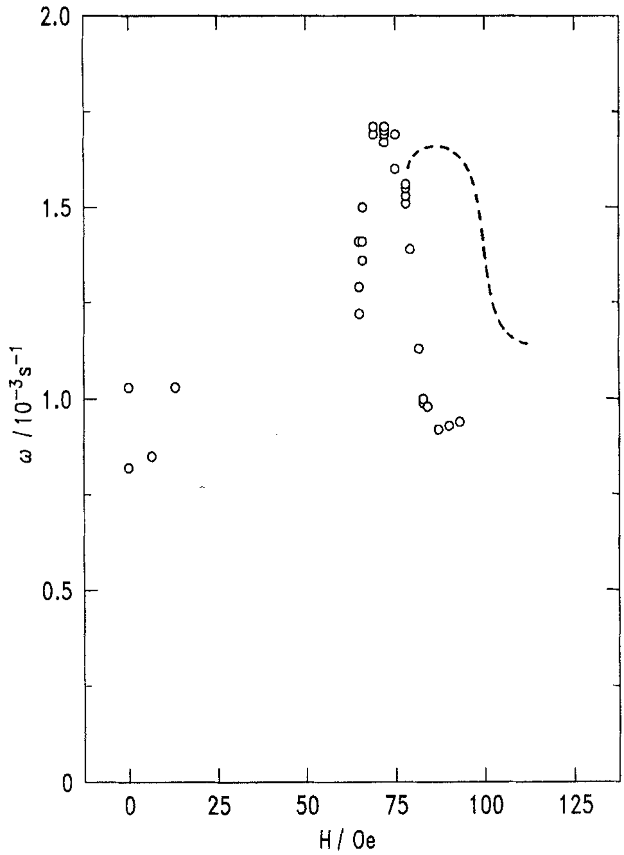

Figure 6. Oscillatory frequencies observed for $\Delta T = -0{\cdot}9°C$ versus applied, vertical magnetic field. The corresponding curve for $\Delta T = -0{\cdot}35°C$ is indicated.

The above observations in the nematic phase imply infinite temporal correlations of the director fluctuations. According to the hypothesis of self-organized criticality [2] we should then expect infinite spatial correlations. We tried to verify this by correlating the signal originating from two points in the sample, and to vary the distance between the points. These experiments gave results of poor reproducibility, and are not included here. All we can say at present is that a nematic sample, in zero field, displays critical temporal fluctuations, as predicted by de Gennes [1], and satisfies one of the conditions for a self-organized, critical phenomenon. Or, expressed differently, it gives an example of fractional brownian motion [13].

In the one constant approximation for the elastic deformations in a nematic substance, the Freederickz field is given by

$$H_c = \frac{\pi}{d}\left(\frac{K}{\bar{\chi}_a}\right)^{1/2}. \tag{8}$$

K is an averaged elastic constant and χ_a the anisotropic diamagnetic susceptibility. d is a geometrical dimension. For our slab geometry we take d to be the short horizintal dimension (3 mm), which together with the tabulated values of K and χ_a [1] gives $H_c \sim 25$ Oe (1 Oe $= 10^{-4}$ T). Figure 5 gives a higher value. One reason for this is, as

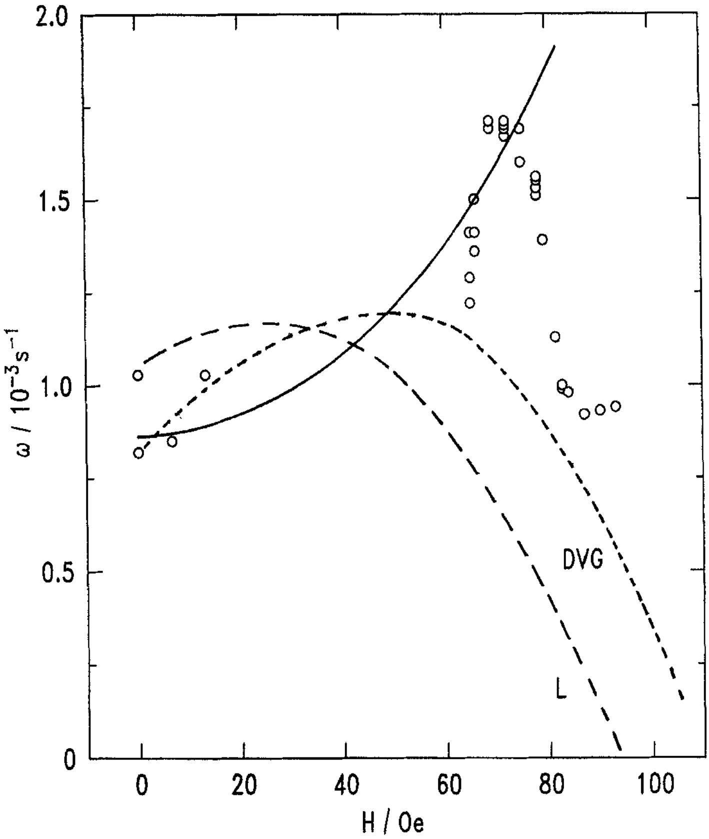

Figure 7. Comparison of data of figure 6 with theoretical models. Curves marked by L and DVG are from [14] and [17], respectively, solid curve is calculated from equation (8) (see text).

remarked above, the ill-defined anchoring conditions at the boundaries. Another reason is the competition between orientation and flow, which may give a strong increase of the field needed to orientate the director, see figure 2 of [12]. It is conceivable that even the fluctuations below the convection threshold ΔT_c may give an apparent enhancement of H_c.

The inverse relaxation time for orientational fluctuations in a nematic is, in the one constant approximation, given by [8]

$$\omega=\frac{1}{\eta}\left[K\left(\frac{\pi}{d}\right)^2+\chi_a H^2\right], \tag{9}$$

where η is an averaged viscosity coefficient. Assuming this formula to give also the frequency of oscillatory states, we find, for $H=0$, $\omega \sim 10^{-3}\,s^{-1}$, as observed. The formula further predicts a dispersion relation $\omega \sim q^2$, as for ferromagnetic spin waves, and a dependence on H that gives $\omega(H_c)=2\omega(0)$.

Another theoretical candidate for explaining our observations is the theory of oscillatory convection in homeotropic nematics heated from below [14–17]. Figure 6 was measured with heating from above, but internal gradients or pretransitional fluctuations might possibly make the formulae relevant. [14–17] all predict a vanishing frequency above $H \sim 100$ Oe. The predictions of [14] and [17] are shown in figure 7. The full-drawn curve is equation (9) with material constants adjusted to give $H_c = 75$ Oe.

It is clear from figure 7 that neither of the theoretical curves give a satisfactory explanation for the observations. The theories may still be relevant, however. The slab geometry used here may, for example, significantly alter the phase diagram and formulae of [14–17].

In seeking a heuristic explanation of the observed oscillations, we turn our attention to the dotted curves in figures 5 and 6. They show that, as we decrease the adverse gradient, i.e. approach the convection threshold located at ~ 1°C, the frequency maximum falls in the middle of the 'Freedericksz curve' for both of the gradient values investigated. The observed displacement of the frequency peak to higher fields, when approaching the convection threshold from below, indicates that the orientational fluctuations are coupled to, and depend on the intensity of pretransitional flow. Recently Allia *et al.* [18] have observed, in light scattering, a well-defined peak of the low frequency spectral density near the threshold field. Possibly their observations and ours are connected.

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