

Critical fluctuations and molecular dynamics at liquid-crystalline phase transitions. I. Theoretical aspects of the nematic–smectic-*A* transition

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A theoretical model is developed for treating molecular dynamics at the nematic–smectic-*A* ($N-S_A$) phase transition, which is frequently second order. This model is motivated by electron-spin-resonance (ESR) spin-relaxation studies of molecular probes. The critical dynamics of the hydrodynamic modes is described in accordance with dynamic scaling arguments of Brochard. Following Zager and Freed, the molecular dynamics of a probe molecule (governed by the molecular orientation and/or rotational diffusion) is assumed to couple to fluctuations in the smectic order parameter, because these molecular properties are a function of the precise location of the probe within the transient smecticlike layer. Two limiting cases of (1) (nearly) free translational diffusion of the probe across the smecticlike layer; and (2) expulsion of the probe to the aliphatic chains with highly hindered diffusion (i.e., jump diffusion) across the smecticlike layer are considered. The relevant spectral density shows critical types of divergence, where the exponent depends strongly on the details of the model. It is found that only the (near) zero-frequency spectral densities can show such divergences. It is pointed out that spectral densities available for spin relaxation do not truly diverge as the $N-S_A$ transition is approached arbitrarily closely, because ultimately motional-narrowing theory will no longer be valid, and fluctuations begin to be frozen on the ESR time scale. This matter is briefly analyzed. Also considered briefly are the effects of anisotropies in the smectic phase and of fluctuations in nematic director near the $N-S_A$ transition.

I. INTRODUCTION

Studies of molecular dynamics at liquid-crystalline phase transitions present a unique opportunity to explore the molecular basis of these very subtle phase transitions. The nematic–isotropic ($N-I$) transition, which is very weakly first order, exhibits quasicritical fluctuations which may be studied by electron-spin resonance (ESR) with spin probes. The nature of the coupling of the molecular motions to these fluctuations has been well explored theoretically,^{1,2} and we report on further detailed experimental studies in paper II.³ The nematic–smectic-*A* ($N-S_A$) transition has been the subject of theoretical and experimental studies, because of its unique properties.^{4–13} It is often second order, but can be weakly first order. Most of the studies are of the static behavior at the $N-S_A$ transition, and they show that the correlation lengths for this transition exhibit an anisotropy and magnitude of their critical exponents that are not consistent with the existing theory for such a phase transition given the expected analogy to that for the lambda transition in helium.

Molecular-dynamics studies at this phase transition are very few,^{14–16} but they provide the opportunity to explore the transition from another vantage point. Of course, it is necessary to explore how the molecular dynamics couples to fluctuations in the smectic order parameter. Zager and Freed¹⁴ have already suggested a mechanism consistent with their initial experimental observations. In this paper, we present a general treatment of the spin relaxation at the $N-S_A$ transition in accordance with that initial work. The

treatment of the critical dynamics is based upon the dynamic scaling arguments of Brochard.⁷ This theory is used for an analysis of extensive ESR studies reported in paper II.³ While we restrict ourselves in this paper to a general theoretical development and to simple limiting cases that can be treated analytically, we describe in paper II the numerical calculations required to more accurately compare theory with experiment. In the latter case, we are able to include the effects of anisotropies in the critical exponents as well as in the dynamic scaling, matters that are only briefly touched on in this paper.

The theoretical model is based on the following observation. ESR probes typically undergo partial expulsion from the orientationally well-ordered aromatic cores of the liquid-crystal molecules toward less-ordered aliphatic regions at the $N-S_A$ transition.^{17,18} Molecular parameters affecting spin relaxation, such as the nematic order parameter of the probe, S , and/or its rotational correlation time τ_R , are themselves affected by the precise location of the probe. The transient formation of smectic layers (cybotactic clusters) as the transition is approached results in a variation of these molecular parameters as a function of probe location within the smectic layer. The smectic layer is described by the density function $\rho(\mathbf{r}, t)$, and near the transition it exhibits fluctuations which are observed to diverge, while its dynamics exhibits critical slowing. Such divergent behavior can then be mirrored in the spin relaxation given that the relevant molecular parameter(s) will depend upon $\rho(\mathbf{r}, t)$. Of course, the probe molecule is diffusing, and if this occurs fast enough, it

can average out such effects. On the other hand, the probe diffusion in an anisotropic fluid will occur relative to a potential $U(\mathbf{r})$ which itself should be dependent upon $\rho(\mathbf{r}, t)$, and this would lead to nonuniform averaging, which is a more formal way of representing the probe expulsion effect noted above. These effects on diffusion are only dealt with in limiting cases in this paper.

The general formalism for calculating the spectral densities near the phase transition is based on our earlier paper,² which dealt with quasicritical orientational fluctuations near the $N-I$ transition. In the same spirit, we assume that there exists a different time scale, the slow cooperative motions associated with the smectic density fluctuations and the rapid rotational motion of the spin probe. Unlike the $N-I$ transition, the observed critical divergence in the zero-frequency spectral densities is rather weak (cf. paper II). This is expected in part, since the modulation of orientational fluctuations associated with probe expulsion ($\approx \Delta S^2 \approx 0.0025$) is weaker than orientational fluctuations at the $N-I$ transition (≈ 0.01).

The theoretical formulation is presented in Sec. II, and some analytic limiting models appear in Sec. III. In Appendix A we discuss, from a multimode viewpoint, the relaxation of the complex smectic order parameter. In Appendix B we consider the range of validity of a motional narrowing approach for ESR (or NMR) in the presence of critical slowing down of the collective fluctuations. Some of the effects of anisotropy of the medium, including fluctuations in the nematic director,⁷ are discussed in Appendix C.

II. THEORETICAL FORMULATION

We first assume that the magnetic and/or relaxation parameter Q (e.g., S or τ_R) may be expanded as a Taylor's series in the local density of the medium. That is,

$$Q(\mathbf{r}) = Q_0 + Q_1 \Delta\rho(\mathbf{r}) + Q_2 [\Delta\rho(\mathbf{r})]^2 + \dots, \quad (1)$$

where

$$\begin{aligned} \Delta\rho(\mathbf{r}) &= \rho(\mathbf{r}) - \rho_0 = \frac{\rho_0}{\sqrt{2}} \operatorname{Re}[\Psi(\mathbf{r})e^{iq_s z}] \\ &= \frac{\rho_0}{\sqrt{2}} |\Psi(\mathbf{r})| \operatorname{Re}(e^{iq_s [z - u(\mathbf{r})]}). \end{aligned} \quad (2)$$

Here, $q_s = 2\pi/d$, where d is the smectic interlayer distance and $\Psi(\mathbf{r})$ is the complex order parameter with phase $\Phi(\mathbf{r}) = q_s u(\mathbf{r})$, where $u(\mathbf{r})$ gives the displacement of the smectic layers in the z direction. Thus fluctuations in $\rho(\mathbf{r})$ will lead to fluctuations in $Q(\mathbf{r})$. We also assume that the translational diffusion of the spin probe obeys the modified diffusion or Smoluchowski equation:

$$\frac{\partial P(\mathbf{r}_B, t)}{\partial t} = -\nabla \cdot \mathbf{D} \cdot \{ \nabla + [\nabla U(\mathbf{r}_B, t)]/kT \} P(\mathbf{r}_B, t), \quad (3)$$

where \mathbf{D} is the diffusion tensor, diagonal in the lab frame such that the z axis is parallel to the mean nematic director $\hat{\mathbf{n}}$. The components of \mathbf{D} parallel and perpendicular to this axis are D_{\parallel} and D_{\perp} , respectively. The appearance of the potential $U(\mathbf{r})$ in this expression represents the "preference" of the probe to be located in the lower density regions of the smec-

tic bilayer. It thus represents the "gradual expulsion" effect discussed in Sec. I. Thus we regard $U(\mathbf{r})$ to be functional of $\Delta\rho(\mathbf{r})$:

$$U = U[\Delta\rho(\mathbf{r})]. \quad (4)$$

Then the dissipative hydrodynamic fluctuations in $\rho(\mathbf{r})$ lead to a time-dependent "potential of mean force" experienced by the spin probe, which enhances its preference for the hydrocarbon chain regions when a smectic cluster forms. This time-dependent Smoluchowski operator can be treated along lines previously developed.² One treats the fluctuations in $\rho(\mathbf{r})$ as a random stochastic process. Thus, a more general diffusion-type of equation, a stochastic-Liouville equation, may be written for the composite or multidimensional Markov process including fluctuations in $\rho(\mathbf{r})$ and the diffusion of the probe. This expression may be more conveniently solved by invoking the different time scales for probe diffusion vs the much slower rate of fluctuations in $\rho(\mathbf{r})$ [i.e., leading to a Born-Oppenheimer-type of separation such that the diffusion of the probe instantaneously adjusts to the fluctuations in $\rho(\mathbf{r})$].¹⁹

The dependence of U on $\Delta\rho(\mathbf{r})$ may not necessarily be expandable in only lowest powers of $\Delta\rho(\mathbf{r})$. Small density changes could lead to severe packing problems, but in the spirit of the mean-field (or Landau) theory near the phase transition we will make this assumption for simplicity. Deep in the smectic phase, when $|\Psi_0| > 0$ and is substantial, one may even contemplate that the hydrocarbon chain region represents such a deep minimum in $U(\mathbf{r})$ that Eq. (3) could be replaced by an expression for "jump diffusion" along the z direction (with simple diffusion in the x and y directions still possible), i.e., it can only jump from the chain region of one smectic layer into the chain region of an adjacent layer. However, if $U(\mathbf{r})$ were to diverge in magnitude then diffusion in the z direction would be prevented. This is analogous to the effect of a divergence (at the $N-S_A$ transition) in the viscosity γ_3 which involves motion of the smectic planes relative to the background liquid.⁴ In dealing with molecular motions it is sounder to attribute such effects to a $U(\mathbf{r})$ rather than to a $D_{\parallel} \rightarrow 0$ (i.e., we have D_{\parallel} proportional to the noncritical portion of the viscosity^{7,8}). Thus, near the transition we shall write for U ,

$$U/kT \approx u_1 \Delta\rho(\mathbf{r}) + u_2 [\Delta\rho(\mathbf{r})]^2 + \dots \quad (5)$$

We may regard this potential as related to the difference in free energy (more precisely the chemical potential) for the probe between the nematic phase and a "smectic phase" (cybotactic cluster) with order parameter $|\Psi|$. To obtain this free-energy contribution, we must average $U(\mathbf{r})$ over \mathbf{r} within a cluster, using Eq. (2), to obtain

$$u_1 \overline{\Delta\rho(\mathbf{r})} = 0 \quad (6)$$

and

$$u_2 \overline{[\Delta\rho(\mathbf{r})]^2} = \frac{1}{4} u_2 \rho_0^2 |\Psi|^2. \quad (7)$$

We thus see that the leading term in the free-energy difference is quadratic in $|\Psi|$, as it is for the pure solvent as required by Landau theory. [Note also that we may relate $U(\mathbf{r})$ to the pair correlation function of the probe, $g(\mathbf{r})$, as $\ln g(\mathbf{r}) = -U(\mathbf{r})/kT$.²⁰]

Let us now first consider the limit where the effects of the potential of mean force $U(\mathbf{r})$ on the diffusive motion may be neglected, so the only effects of critical fluctuations will arise as a consequence of Eq. (1). Then spin relaxation will depend upon the correlation function $\langle \Delta Q(\mathbf{r}_B, t) \Delta Q(\mathbf{r}_B, t=0) \rangle$, which in turn depends upon the correlation function for the fluctuations in the smectic order parameter Ψ :

$$\langle \Delta Q(\mathbf{r}_B, t) \Delta Q(\mathbf{r}_B, t=0) \rangle \propto \langle \Psi^*(\mathbf{r}_B, t) \Psi(\mathbf{r}_B, 0) \rangle + \dots, \quad (8)$$

where \dots denotes higher-order terms, \mathbf{r}_B is the location of the probe, and $\Delta Q = Q(\mathbf{r}) - Q_0$. For a nondiffusing probe, we can use the result of Jähnig and Brochard (JB) for the q th mode of fluctuation:⁸

$$\langle \Psi^*(\mathbf{q}, t) \Psi(\mathbf{q}, 0) \rangle = \langle |\Psi(\mathbf{q})|^2 \rangle e^{-t/\tau_q}, \quad (9)$$

where $\Psi(\mathbf{q}, t)$ is the Fourier transform of $\Psi(\mathbf{r}, t)$. The relaxation time τ_q is expected to obey a scaling equation of the form $\tau_q^{-1} = \xi_{\parallel}^z f(q_{\parallel} \xi_{\parallel}, q_{\perp} \xi_{\perp})$ with $\xi_{\parallel} \sim \xi_{\perp} = \xi$ and $z \approx 3/2$. For $q\xi \gg 1$, τ_q is independent of ξ and $f \sim (q\xi)^{-3/2}$. JB introduced a simple interpolation formula for τ_q that satisfies dynamic scaling:

$$\tau_q = \tau_m / (1 + q_{\perp}^2 \xi_{\perp}^2 + q_{\parallel}^2 \xi_{\parallel}^2)^x. \quad (10)$$

In Eq. (9), the mean-square displacement in order parameter is

$$\langle |\Psi(\mathbf{q})|^2 \rangle = \frac{k_b T}{2A} \frac{1}{(1 + q_{\perp}^2 \xi_{\perp}^2 + q_{\parallel}^2 \xi_{\parallel}^2)^x} \equiv \alpha_q^{-1}. \quad (11)$$

Also, ξ_{\parallel} and ξ_{\perp} are the coherence lengths parallel and perpendicular to the z axis (referring to the nematic director $\hat{\mathbf{n}}$), respectively, and q_{\parallel} and q_{\perp} are the respective components of \mathbf{q} . V is the sample volume, while A is the coefficient in the term quadratic in $\Psi(\mathbf{r})$ in the Landau expansion of the smectic free energy.²¹ Using the analogy to the λ transition in helium,⁴⁻⁸ one expects ξ_{\perp} and ξ_{\parallel} to diverge similarly as $\xi \propto (T - T_{NS_A})^{-2/3}$; also, $A \propto \xi^{-2+\eta}$ ($\eta \approx 0.04$), and $\tau_m \propto \xi^{3/2} \propto (T - T_{NS_A})^{-1}$. According to dynamic scaling arguments,^{7,8,22} one must have $x = 3/4$ in Eq. (10). Although the actual case for the $N-S_A$ transition is more complicated, exhibiting anisotropic exponents, we utilize the helium analogy in this paper for convenience in presentation, but in paper II for comparison with actual experiment we take all these complications into consideration.

More precisely, we have

$$\langle \Delta Q(\mathbf{r}_B, t) \Delta Q(\mathbf{r}_B, 0) \rangle \propto Q_1^2 C(t) + \dots, \quad (12a)$$

where

$$C(t) \equiv \langle \Delta \rho(\mathbf{r}_B) \Delta \rho(\mathbf{r}_{B,0}) \rangle / \rho_0^2 \\ = \frac{1}{2} \langle \text{Re} [\Psi(\mathbf{r}_B) e^{i\mathbf{q} \cdot \mathbf{r}_B}] \times \text{Re} [\Psi(\mathbf{r}_{B,0}) e^{i\mathbf{q} \cdot \mathbf{r}_{B,0}}] \rangle, \quad (12b)$$

where we have let \mathbf{r}_B be the position vector of the probe at time t and $\mathbf{r}_{B,0}$ its position at $t=0$. Also, $\mathbf{q}_s = q_s \hat{\mathbf{k}}$. This may be written as

$$\rho_0^2 C(t) = \int P_{\text{eq}}(\Delta \rho(\mathbf{r}_0), \mathbf{r}_B) \\ \times P(\Delta \rho(\mathbf{r}_0), \mathbf{r}_{B,0} | \Delta \rho(\mathbf{r}), \mathbf{r}_B, t) \\ \times \Delta \rho(\mathbf{r}_B) \Delta \rho(\mathbf{r}_{B,0}) d\mathbf{r}_B d\mathbf{r}_{B,0} d\Delta \rho(\mathbf{r}) d\Delta \rho(\mathbf{r}_0), \quad (13)$$

where

$$P_{\text{eq}}(\Delta \rho(\mathbf{r}_0), \mathbf{r}_{B,0}) \approx P_{\text{eq}}(\Delta \rho(\mathbf{r}_0)) P_{\text{eq}, \Delta \rho(\mathbf{r}_0)}(\mathbf{r}_{B,0}) \quad (14)$$

is the joint equilibrium distribution function for the density fluctuations in the fluid and for the location of the probe molecule. The approximate form² assumes that the probe does not significantly perturb the density fluctuations, but the location of the probe is, in general, sensitive to the instantaneous value of the density fluctuations. The joint conditional probability density for density fluctuations and probe locations obeys in our "Born-Oppenheimer-type" approximation

$$P(\Delta \rho(\mathbf{r}_0), \mathbf{r}_B, 0 | \Delta \rho(\mathbf{r}), \mathbf{r}_B, t) \\ \approx P(\Delta \rho(\mathbf{r}_0) | \Delta \rho(\mathbf{r}), t) P_{\Delta \rho(\mathbf{r})}(\mathbf{r}_B, 0 | \mathbf{r}_B, t), \quad (15)$$

where the conditional probability that the probe is located at \mathbf{r}_B at time t given it was at $\mathbf{r}_{B,0}$ at $t=0$ is again dependent upon the instantaneous $\Delta \rho(\mathbf{r})$. In the absence of density fluctuations we have

$$P(\mathbf{r}_{B,0} | \mathbf{r}_B, t) = \sum_{\mathbf{q}} |\mathbf{r}_{B,0}, \mathbf{q}\rangle \exp[-(D_{\parallel} q_{\parallel}^2 + D_{\perp} q_{\perp}^2)t] \\ \times \langle \mathbf{r}_B, \mathbf{q} | \\ \rightarrow \int d\mathbf{q} |\mathbf{r}_{B,0}, \mathbf{q}\rangle \exp[-(D_{\parallel} q_{\parallel}^2 + D_{\perp} q_{\perp}^2)t] \\ \times \langle \mathbf{r}_B, \mathbf{q} |, \quad (16)$$

where the ket $|\mathbf{r}_B, \mathbf{q}\rangle$ is given by

$$|\mathbf{r}_B, \mathbf{q}\rangle = e^{-i\mathbf{q} \cdot \mathbf{r}_B} / V^{1/2} \quad (17a)$$

and

$$|P_{\text{eq}, \mathbf{r}_B}\rangle = |\mathbf{r}_B, \mathbf{q} = 0\rangle = V^{-1/2}. \quad (17b)$$

Equation (16) is the solution to Eq. (3) with $U=0$. When Eq. (5) is used for Eq. (3), then the conditional probability for \mathbf{r}_B becomes a function of $\Delta \rho(\mathbf{r})$. Rather than attempt a complete solution of this equation at present we shall first take Eq. (5) to lowest order in $\Delta \rho(\mathbf{r})$. Then we shall utilize a "strong-collision type" of approximation² to write

$$P_{\text{eq}, \Delta \rho(\mathbf{r}_0)}(\mathbf{r}_{B,0}) \approx P_{\text{eq}}(\mathbf{r}_{B,0}) [1 - u_1 \Delta \rho(\mathbf{r}_{B,0}) + \dots] \quad (18)$$

and

$$P_{\Delta \rho(\mathbf{r})}(\mathbf{r}_{B,0} | \mathbf{r}_B, t) \approx P(\mathbf{r}_{B,0} | \mathbf{r}_B, t) \\ \times [1 - u_1 \Delta \rho(\mathbf{r}_B) + \dots], \quad (19)$$

where the probabilities on the right-hand side of Eqs. (18) and (19) are given, respectively, by Eqs. (17b) and (16). While Eq. (19) cannot be regarded as rigorous, it does indicate the magnitude of the contributions of the density fluctuations to the dynamics of the probe diffusion, in the limit of small density fluctuations.

Now $P(\Delta\rho(\mathbf{r}_0)|\Delta\rho(\mathbf{r}),t)$ is a multidimensional joint probability distribution for the values of $\Delta\rho$ at each \mathbf{r} . This is best transformed to the equivalent normal-mode distribution in \mathbf{q} space. This is accomplished, in the usual manner, by Fourier transforming the order parameter $\Psi(\mathbf{r})$. However, since $\Psi(\mathbf{r})$ is complex, one may consider it as a two-component order parameter consisting of $\text{Re } \Psi(\mathbf{r})$ and $\text{Im } \Psi(\mathbf{r})$. Jähnig and Brochard⁸ invoke the simplifying assumption that the real and imaginary parts of $\Psi(\mathbf{r})$ are uncorrelated in their fluctuations. We follow a different approach here. We first consider $\Psi(\mathbf{r})$ as a two-dimensional vector in the complex plane. Then we transform its components as

$$\Psi_R(\mathbf{q}) \equiv \frac{1}{V} \int [\text{Re } \Psi(\mathbf{r})] e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \equiv \langle \text{Re } \Psi(\mathbf{r}) | \mathbf{r}, \mathbf{q}_j \rangle, \quad (20a)$$

$$\Psi_I(\mathbf{q}) \equiv \frac{1}{V} \int [\text{Im } \Psi(\mathbf{r})] e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \equiv \langle \text{Im } \Psi(\mathbf{r}) | \mathbf{r}, \mathbf{q}_j \rangle, \quad (20b)$$

and we let

$$\Psi_{\pm}(\mathbf{q}) \equiv \Psi_R(\mathbf{q}) \pm i\Psi_I(\mathbf{q}). \quad (21)$$

Now from Eq. (2) we have

$$\begin{aligned} \Delta\rho(\mathbf{r}) &= \frac{\rho_0}{2\sqrt{2}} [\Psi_+(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}} + \Psi_-(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}] \\ &= \frac{\rho_0}{\sqrt{2}} \text{Re} \sum_{\mathbf{q}} \Psi_+(\mathbf{q}) e^{-i(\mathbf{q}+\mathbf{q}_s)\cdot\mathbf{r}}, \end{aligned} \quad (22)$$

where we have used

$$\begin{aligned} \rho_0^2 C(t) &= \sum_{\mathbf{q}_k} \sum_{N,M} \langle P_{\text{eq}\Delta\rho}(\mathbf{r}_B) | \left[\langle P_{\text{eq}}(\Delta\rho(\mathbf{r})) | \Delta\rho(\mathbf{r}_B) | \mathbf{r}_B, \mathbf{q}_k \rangle e^{-(D_{\parallel}q_{\parallel}^2 + D_{\perp}q_{\perp}^2)t} \prod_{\mathbf{q}} |Y_N^M(\Psi(\mathbf{q}))\rangle \right] \\ &\quad \times e^{-W_{\mathbf{q},N}^M t} [\langle Y_N^M(\Psi_0(\mathbf{q})) | \langle \mathbf{r}_{B,0}, \mathbf{q}_k | \Delta\rho(\mathbf{r}_B) | P_{\text{eq}}(\Delta\rho(\mathbf{r})) | P_{\text{eq}}(\mathbf{r}_{B,0}) \rangle]]. \end{aligned} \quad (25)$$

In writing Eq. (25) we have considered only the leading term in Eqs. (18) and (19) in the spirit of obtaining just the lowest-order contribution in $\Delta\rho(\mathbf{r})$ to $C(t)$. We now use the Fourier inverse of Eqs. (20) to write

$$\begin{aligned} \Delta\rho(\mathbf{r}_B) &= \frac{\rho_0}{\sqrt{2}} \text{Re} \sum_{\mathbf{q}} \Psi_+(\mathbf{q}) e^{i(\mathbf{q}+\mathbf{q}_s)\cdot\mathbf{r}_B} \\ &\rightarrow \frac{V}{(2\pi)^3} \frac{\rho_0}{2\sqrt{2}} \int |\Psi(\mathbf{q})| e^{i\phi(\mathbf{q})} e^{i(\mathbf{q}+\mathbf{q}_s)\cdot\mathbf{r}_B} d\mathbf{q} + \text{c.c.} \end{aligned} \quad (26)$$

We evaluate Eq. (25) by first noting (letting $\mathbf{q}' = \mathbf{q} + \mathbf{q}_s$)

$$\begin{aligned} \langle P_{\text{eq}}(\mathbf{r}_B) | e^{i\mathbf{q}'\cdot\mathbf{r}_B} | \mathbf{r}_B, \mathbf{q}_k \rangle \\ &= \frac{1}{V} \int d^3\mathbf{r}_B \exp[-i(\mathbf{q}_k - \mathbf{q}')\cdot\mathbf{r}_B] \\ &= \frac{(2\pi)^3}{V} \delta(\mathbf{q}_k - \mathbf{q}'), \end{aligned} \quad (27)$$

$$\Psi_R^*(\mathbf{q}) = \Psi_R(-\mathbf{q}), \quad (23a)$$

$$\Psi_I^*(\mathbf{q}) = \Psi_I(-\mathbf{q}), \quad (23b)$$

which follows from the fact that both $\text{Re } \Psi(\mathbf{r})$ and $\text{Im } \Psi(\mathbf{r})$ are real quantities. We now let $\Psi_{\pm}(\pm\mathbf{q}) = |\Psi(\mathbf{q})| e^{\pm i\phi(\mathbf{q})}$. It also follows that $\Psi_+^*(\mathbf{q}) = \Psi_-(-\mathbf{q})$. We then consider that since $\langle |\Psi(\mathbf{q})|^2 \rangle = \langle \Psi_+(\mathbf{q})\Psi_-(-\mathbf{q}) \rangle$, and is given by Eq. (11), while the phase factor $\langle |q_s u(\mathbf{q})|^2 \rangle = 0$ above the phase transition, then it will be sufficient to allow $\phi_{\mathbf{q}} \equiv \tan^{-1}[\text{Im } \Psi_+(\mathbf{q})/\text{Re } \Psi_-(\mathbf{q})]$ to be random. Thus the fluctuations of the real and imaginary components of the vector $\Psi(\mathbf{q})$ may be regarded as a diffusion in the complex plane consistent with Eq. (9), and such that it is a one-sided Gaussian with respect to $|\Psi(\mathbf{q})|$, but all values of $\phi(\mathbf{q})$ are equally probable. This is developed in Appendix A. We find that each independent \mathbf{q} mode obeys the following conditional probability:

$$\begin{aligned} P(\Psi_0(\mathbf{q})|\Psi(\mathbf{q}),t) &= \sum_{N,M} |Y_N^M(\Psi(\mathbf{q}))\rangle \\ &\quad \times \exp(-W_{\mathbf{q},N}^M t) \langle Y_N^M(\Psi_0(\mathbf{q})) |. \end{aligned} \quad (24)$$

Equation (24) expresses the conditional probability in terms of eigenkets $|Y_N^M(\Psi(\mathbf{q}))\rangle$ given by Eq. (A10) and eigenvalues $W_{\mathbf{q},N}^M$ given by Eq. (A15). An expression for the equilibrium probability distribution, $P_{\text{eq}}(\Psi(\mathbf{q}))$ is given by Eq. (A12). Then, the complete probability distribution involving all the independent \mathbf{q} modes, i.e., $\mathbf{P}(\Psi(\mathbf{q}),t)$ is given by

$$\mathbf{P}(\Psi(\mathbf{q}),t) = \prod_{\mathbf{q}} P(\Psi(\mathbf{q}),t). \quad (24a)$$

Thus Eq. (13) becomes

and then by using the limiting integral form of Eq. (26) to obtain

$$\begin{aligned} 4C(t) &= \sum_{\mathbf{q}_k} \sum_{N,M} |\langle Y_0^0(\Psi(\mathbf{q}_k - \mathbf{q}_s))\Psi(\mathbf{q}_k - \mathbf{q}_s) \\ &\quad \times |Y_N^M(\Psi(\mathbf{q}_k - \mathbf{q}_s))\rangle|^2 \\ &\quad \times \exp[-(W_{\mathbf{q}_k - \mathbf{q}_s, N}^M + D_{\parallel}q_{k,\parallel}^2 + D_{\perp}q_{k,\perp}^2)t]. \end{aligned} \quad (28)$$

It follows from the property of the Y_N^M functions (see Appendix A) that only the term of $M=1, N=0$ contributes for each \mathbf{q}_k . Then we obtain (dropping the subscript k)

$$C(t) = \sum_{\mathbf{q}} C_{\mathbf{q}}(t) = \frac{V}{(2\pi)^3} \int_0^{q_c} C_{\mathbf{q}}(t) d^3\mathbf{q}, \quad (29a)$$

where

$$4C_{\mathbf{q}}(t) = \alpha_{\mathbf{q}-\mathbf{q}_s}^{-1} \exp[-(\tau_{\mathbf{q}-\mathbf{q}_s}^{-1} + D_{\parallel}q_{\parallel}^2 + D_{\perp}q_{\perp}^2)t]. \quad (29b)$$

III. LIMITING MODELS

The form of $C(t)$ and the associated spectral density

$$J(\omega) = \text{Re} \int_0^\infty C(t) e^{-i\omega t} dt \quad (30)$$

is complicated. We therefore consider two limiting cases here, and defer to paper II the numerical solution of Eq. (29). In the first we use a "one-constant" or isotropy approximation such that $\xi_{\parallel} = \xi_{\perp} = \xi$ and we let $x = 1$ in Eq. (10) while $D_{\parallel} = D_{\perp} = D$, but we ignore averaging by diffusion through the smectic layer by letting $q_s \rightarrow 0$ (i.e., $D_{\parallel} q_s^2 \tau_m \rightarrow 0$). Then the integrals are readily evaluated (in the limit $q_c \rightarrow \infty$) to yield

$$4C(t) = \frac{Mk_b T}{4\pi^{3/2}} \frac{\tau_m^{1/2}}{\xi} e^{-t/\tau_m} \left[t^{-1/2} - (\pi/\tau_m)^{1/2} \times (e^{+t/\tau_m}) \text{erfc}[(t/\tau_m)^{1/2}] \right], \quad (31a) \quad \text{and}$$

$$4J(\omega) = \frac{Mk_b T}{4\pi} \xi \left(\frac{D[1 - \sqrt{z/2} [(1 + \omega^2 \tau_m^2)^{1/2} + 1]^{1/2}] + (\omega \xi^2 / \sqrt{2}) \sqrt{z} [(1 + \omega^2 \tau_m^2)^{1/2} - 1]^{1/2}}{\omega^2 \xi^4 + D^2} \right), \quad (32b)$$

where

$$\tau'_m = z\tau_m \quad (33a)$$

and

$$z \equiv (1 + D\tau_m/\xi^2)^{-1}. \quad (33b)$$

Under the above approximations, the role of diffusion is confined to the motions which carry the probe from one smecticlike cluster to another. It is seen that the deviation of z from unity is a measure of the importance of translational diffusion. In fact, we can regard the ratio $D\tau_m/\xi^2$ in z to be equal to τ_m/t_ξ , where t_ξ is the time a Brownian particle will take to diffuse a distance equal to $\sqrt{6}\xi$, i.e., to diffuse out of the pretransitional smectic cluster (see also Appendix C). When $D\tau_m/\xi^2 \gg 1$ (i.e., $z \ll 1$) this is the dominant relaxation; When $D\tau_m/\xi^2 \ll 1$ (i.e., $z \approx 1$) the relaxation of the smectic cluster itself, governed by τ_m , is dominant.

If we now let $\omega\tau_m \rightarrow 0$, Eq. (32b) becomes

$$4J(0) = \frac{Mk_b T}{4\pi} \frac{\tau'_m}{\xi} (1 + z^{1/2})^{-1}. \quad (34)$$

Thus when $z \rightarrow 1$, $J(0) \propto \tau_m/\xi \propto \xi^{-1/2}$, which is in agreement with the experimental results (cf. paper II). When, however $z \ll 1$, then $4J(0) \cong (Mk_b T/4\pi D)\xi \propto \xi^1$, which shows a stronger divergence.

When we let $\omega \gg \tau_m^{-1}$, D/ξ^2 , one has

$$4J(\omega) = \frac{Mk_b T}{4\sqrt{2\pi}} \left(\frac{\tau'_m}{\omega} \right)^{1/2} \xi^{-1}. \quad (35)$$

Thus, the behavior of the high-frequency limiting form of $J(\omega)$ given by Eq. (35) also depends upon z . In the limit $z \approx 1$, $J(\omega) \propto \tau_m^{1/2}/\xi \propto \xi^{-1/4}$, so that it goes to zero slowly as $T \rightarrow T_{NS}$. In the other limit, $z \ll 1$,

where $M = (2A\xi^2)^{-1}$, and

$$4J(\omega) = \frac{Mk_b T}{4\sqrt{2\pi}} \frac{\tau_m}{\xi} \left(\frac{1}{1 + [1 + (\omega\tau_m)^2]^{1/2}} \right)^{1/2} \quad (31b)$$

for the case of $D = 0$. (The result for $\xi_{\parallel} \neq \xi_{\perp}$ is considered in Appendix C.) For finite D , these expressions become

$$4C(t) = \frac{Mk_b T}{4\pi^{3/2}} \left[\left(\frac{\tau'_m}{t\xi^2} \right)^{1/2} e^{-t/\tau_m} - \frac{\sqrt{\pi}}{\xi} e^{Dt/\xi^2} \text{erfc}(t/\tau'_m)^{1/2} \right] \quad (32a)$$

and

$$4J(\omega) \approx \frac{Mk_b T}{4\sqrt{2\pi}} (\omega D)^{-1/2}$$

and it shows no significant critical behavior. This important difference between $J(0)$ which can diverge, and $J(\omega)$ for high frequencies which does not, also emerges from the detailed numerical calculations (cf. paper II).

When we introduce higher-order terms in the expansion of the relaxation parameter [Eq. (1)] or else in the probability distributions Eqs. (18) and (19) for probe diffusion, then the next order terms will involve the time correlation function of $[\Delta\rho(\mathbf{r})]^2$. This is examined in Appendixes A and C where terms of this order are found to make a contribution to $J(0)$ which goes to zero approximately as $\xi^{-1/2}$, and are thus unimportant. Thus, to the order considered here, it is the lowest-order term, and the (near)-zero frequency spectral density at that, which can be effective in producing a critical divergence for this limiting case.

For the second case, we only solve for $\omega = 0$, but retain the asymmetries and finite q_s . Also, the effects of a finite q_c are included. In particular, we set the maximum in $|q_{\perp}|$ as $q_{\perp,c}$, while $q_{\parallel,c}$ is taken to be of order q_s . We again let $x = 1$. We then consider the limiting case, which becomes valid close enough to the phase transition, of

$$D_{\perp} \tau_m / \xi_{\perp}^2, \quad D_{\parallel} \tau_m / \xi_{\parallel}^2 \ll 1, \quad (36)$$

i.e., the terms on the left-hand side of Eq. (36) go to zero as $\tau_m / \xi^2 \propto \xi^{-1/2}$. One can write [cf. Appendix C, Eqs. (C2)]

$$4J(\omega) \approx \frac{k_b T \tau_m}{A(2\pi)^2 \xi_{\perp}^2 \xi_{\parallel}} \text{Re} \int_0^{2q_s \xi_{\parallel}} dP_{\parallel} \int_0^{q_{\perp,c} \xi_{\perp}} P_{\perp} dP_{\perp} \times (1 + P_{\perp}^2 + P_{\parallel}^2)^{-1}$$

$$\begin{aligned} & \times (\omega\tau_m + 1 + P_{\perp}^2 + P_{\parallel}^2 + q_s^2 D_{\parallel} \tau_m \\ & - 2q_s D_{\parallel} \tau_m P_{\parallel} / \xi_{\parallel})^{-1}. \end{aligned} \tag{37}$$

One can show that for the second inequality in Eq. (36), that $(2q_s D_{\parallel} \tau_m P_{\parallel} / \xi_{\parallel}) \ll (P_{\parallel}^2 + q_s^2 D_{\parallel} \tau_m)$ over the full range of values of P_{\parallel} . So we ignore this term in the integration. We now let $q_s \xi_{\parallel}$ and $q_{\perp, c} \xi_{\perp} \rightarrow \infty$ and we obtain

$$4J(0) = \frac{M_T k_b T \tau_m}{4\pi \xi_{\parallel}} \frac{\sqrt{1+c}-1}{c}, \tag{38}$$

where

$$c = q_s^2 D_{\parallel} \tau_m \tag{39}$$

and

$$M_T^{-1} = 2A \xi_{\perp}^2. \tag{40}$$

Equation (38) is for the case when we ignore relaxation by diffusion from one smectic cluster to another. Instead, it retains the averaging effect through the smectic layer, as measured by

$$c = (2\pi)^2 D_{\parallel} \tau_m / d^2 \equiv 2\pi^2 \tau_m / t_d,$$

where t_d is the time it takes to diffuse through the smectic layer of thickness d , vs the relaxation of the smectic layers. As $c \rightarrow 0$, one has

$$4J(0) \approx (M_T k_b T / 8\pi) \tau_m / \xi_{\parallel} \propto \xi^{1/2},$$

which is equivalent to the case of Eq. (34), in the limit that the dominant averaging is by relaxation of the smectic clusters. As $c \rightarrow \infty$,

$$4J(0) \approx (M_T k_b T / 4\pi q_s D_{\parallel}^{1/2}) \tau_m^{1/2} / \xi \propto \xi^{-1/4},$$

so it goes to zero as $T \rightarrow T_{NA}$. Clearly, rapid averaging by probe diffusion through the smectic layer removes the sensitivity to the density variation within the smectic layer within our lowest-order theory.

It is difficult to predict analytically the simultaneous effects of diffusional averaging both through the smectic layer and from one smectic cluster to another, as well as the effect of anisotropies in diffusion tensor and in correlation lengths and exponents (as well as an $x = 3/4$), but the numerical calculations in paper II show that for realistic values of the parameters the effect of diffusional averaging through the smectic layer does suppress the critical divergence.

There is, however, another point of view, or limiting case that dramatizes the expulsion effect which has not played a significant role to lowest order of U in $\rho(\mathbf{r})$. It was briefly noted in Sec. II, and is the case when the probe is confined to the chain region, where it can only jump from the chain region of one smectic layer into that of an adjacent layer. In this case, there can be no averaging of diffusion across the smectic layer, since $P_{\mathbf{c}\mathbf{q}, \Delta\rho(\mathbf{r}_0)}(\mathbf{r}_{B,0})$ [cf. Eq. (14)] is heavily weighted in the chain region even for very small $\Delta\rho(\mathbf{r}_0)$. In this case, Eqs. (31)–(35) constitute the correct solution. [Another way to look at this limit is to recognize that the parameter $Q(\mathbf{r}_B, t)$ depends only upon whether the probe is in the transient smectic cluster or not. If it is, its position rapidly readjusts to the hydrocarbon region. The measure of smectic layering is just $\Psi(\mathbf{r})$ and not $\Delta\rho(\mathbf{r})$. Thus one is interested in the correlation function

$\langle \Psi(\mathbf{r}, t) \Psi(\mathbf{r}, 0) \rangle$ rather than Eq. (12b). However, the two become equivalent in the limit $q_s \rightarrow 0$.] This case is considered in detailed numerical calculations in paper II, and, for realistic values of the parameters, yield significant critical exponents for $J(0)$ that depend significantly on diffusion tensor, coherence length, and exponents, as well as dynamic scaling of τ_m and the associated anisotropies. Values for the critical exponent for $J(0)$ range from about $-1/3$ to about $-1/2$ for this model for a range of relevant values of the parameters.

Clearly, a model that is intermediate between complete diffusional averaging and no such averaging through the smectic layer would be worthy of further study. Some partial averaging would be expected to reduce somewhat the critical exponents obtained in the limit of no averaging.

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APPENDIX A: DIFFUSIVE RELAXATION OF THE FOURIER COMPONENTS OF A COMPLEX ORDER PARAMETER

Jähnig and Brochard⁸ assumed a simple relaxation behavior of the order parameter in Fourier space, and then applied dynamic scaling arguments. We shall consider this relaxation in a form appropriate to obtain the dynamical averaging that is needed in the present work. Thus we recognize that above T^* , the collective mode $\Psi(\mathbf{q})$ is constrained to perform fluctuations with mean square given by Eq. (11), but the phase $\phi_{\mathbf{q}} \equiv q_s u_{\mathbf{q}}$ is arbitrary. We wish to express this by a diffusion equation for $\Psi(\mathbf{q}) = |\Psi(\mathbf{q})| e^{iq_s u_{\mathbf{q}}}$. We regard this as a diffusion in the complex plane with polar coordinates $\rho \rightarrow |\Psi(\mathbf{q})|$ and $\phi \rightarrow u_{\mathbf{q}}$; i.e., we let $P(\Psi(\mathbf{q}), t)$ obey a diffusion equation subject to the collective potential $V(|\Psi(\mathbf{q})|)$. That is,

$$\frac{\partial P(\Psi(\mathbf{q}), t)}{\partial t} = -\Gamma_{\Psi(\mathbf{q})} P(\Psi(\mathbf{q}), t). \tag{A1}$$

Here,

$$\Gamma_{\Psi(\mathbf{q})} = -D_{\Psi(\mathbf{q})} [\nabla^2 + \nabla \cdot (\nabla \hat{V}(\mathbf{q}))], \tag{A2}$$

where

$$\hat{V}(\mathbf{q}) \equiv V(|\Psi(\mathbf{q})|) / k_b T, \tag{A3}$$

and ∇^2 and ∇ are expressed in planar polar coordinates. The diffusion operator becomes

$$\begin{aligned} -\Gamma_{\Psi(\mathbf{q})} = D_{\Psi(\mathbf{q})} & \left[\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \left(\frac{\partial \hat{V}(\mathbf{q})}{\partial \rho} \right) \frac{\partial}{\partial \rho} \right. \\ & \left. + \frac{1}{\rho} \left(\frac{\partial \hat{V}(\mathbf{q})}{\partial \rho} \right) + \frac{\partial^2 \hat{V}(\mathbf{q})}{\partial \rho^2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right]. \end{aligned} \tag{A4}$$

Note that Eq. (A1) neglects streaming terms which should lead to propagation effects in the smectic phase. This will not

be important at the $N-S_A$ phase transition, cf. Ref. 21. Deeper into the smectic phase, the propagation of second sound becomes significant, but should be much less important (cf. paper II) for spin probes than the expulsion effect that couples to the fluctuations of $\Psi(\mathbf{r}, t)$, which is the basis of our present model. Now in accordance with Eq. (11) [or more precisely, using the free-energy terms quadratic in $|\Psi(\mathbf{q})|$ (cf. Refs. 7 and 8)], we let $\tilde{V}(\mathbf{q}) = \alpha_q |\Psi(\mathbf{q})|^2 = \alpha_q \rho^2$. Then we have

$$-\Gamma_\rho = D_{\Psi(\mathbf{q})} \left(\frac{d^2}{d\rho^2} + \frac{1}{\rho} \frac{d}{d\rho} + 2\alpha_q \rho \frac{d}{d\rho} + 4\alpha_q - \frac{M^2}{\rho^2} \right) \quad (\text{A5})$$

after separating out the ϕ dependence. This diffusion operator can be symmetrized by the transformation

$$\tilde{\Gamma}_\rho = e^{\alpha_q \rho^2/2} \Gamma_\rho e^{-\alpha_q \rho^2/2} \quad (\text{A6})$$

and becomes

$$-\tilde{\Gamma}_\rho y^M(\rho) = D_{\Psi(\mathbf{q})} \left(\frac{d^2}{d\rho^2} + \frac{1}{\rho} \frac{d}{d\rho} - \frac{M^2}{\rho^2} - 2\alpha_q \rho + 4\alpha_q \right) y(\rho). \quad (\text{A7})$$

Instead of solving for the eigenfunctions y^M of this operator, we solve for functions $v(\rho) = \rho^{1/2} y^M(\rho)$, which yields the standard differential form:

$$\frac{d^2 v}{dz^2} + \frac{1 - 4M^2}{4z^2} + 2 - z^2 v = E v, \quad (\text{A8})$$

where we have let $z = \alpha_q^{1/2} \rho$, with eigenvalue E . Its solutions are in terms of generalized Laguerre polynomials,²³ $L_N^M(z^2)$, leading finally to the eigenfunctions:

$$y_N^M(\rho) = [z \alpha_q N! / (N + |M|)!]^{1/2} e^{-\alpha_q \rho^2/2} \times (\alpha_q^{1/2} \rho)^{|M|} L_N^{|M|}(\alpha_q \rho^2). \quad (\text{A9})$$

The solution to the symmetrized $\Gamma_{\Psi(\mathbf{q})}$ including the ϕ dependence is

$$Y_N^M(\Psi(\mathbf{q})) = y_N^M(\Psi(\mathbf{q})) e^{iM\phi} (2\pi)^{1/2}, \quad (\text{A10})$$

and its eigenvalues are

$$W_{q,N}^M = (\tau_q^{-1})_N^M = 2\alpha_q D_{\Psi(\mathbf{q})} (2N + |M|), \quad N \geq 0. \quad (\text{A11})$$

The equilibrium probability distribution function is

$$P_{\text{eq}}(\Psi(\mathbf{q})) = [Y_0^0(\Psi(\mathbf{q}))]^2 = \frac{\alpha_q}{\pi} e^{-\alpha_q |\Psi(\mathbf{q})|^2}, \quad (\text{A12})$$

and the conditional probability distribution is

$$P(\Psi_0(\mathbf{q}) | \Psi(\mathbf{q}), t) = \sum_{N,M} |Y_N^M(\Psi(\mathbf{q}))\rangle e^{-W_{q,N}^M t} \langle Y_N^M(\Psi_0(\mathbf{q}))| \quad (\text{A13})$$

[which is Eq. (24)].

The requirements that these expressions yield Eqs. (9)–(11) are found from the derivation [cf. Eq. (27)] to yield

$$(\tau_q^{-1})_0^1 = 2\alpha_q D_{\Psi(\mathbf{q})} = \tau_q^{-1}, \quad (\text{A14})$$

where τ_q^{-1} is given by Eq. (10). Thus

$$W_{q,N}^M = \tau_q^{-1} (2N + |M|). \quad (\text{A15})$$

The dynamical properties of the complex order parameter $\Psi(\mathbf{q})$ are thus seen to be similar, but not identical, to a simple order parameter which can be represented by a Gaussian distribution and Hermite polynomial eigenfunctions.²

Utilizing these expressions, it is now possible to calculate general correlation functions of type

$$\langle f_i^*(\Psi(\mathbf{r})) f_0(\Psi(\mathbf{r})) \rangle,$$

where $f_i(\Psi(\mathbf{r}))$ is some function of $\Psi(\mathbf{r})$ at time t . The calculation where $f_i(\Psi(\mathbf{r})) = \Psi(\mathbf{r})$ and $|\Psi(\mathbf{r})|$ have been discussed in Secs. II and III. They require calculation of the matrix elements of $\Psi(\mathbf{r})$, which have been given elsewhere in a slightly different context.^{24,25} By similar means we can calculate the correlation function of $|\Psi(\mathbf{r})|^2$. The correlation functions in Sec. II involve just the single excitation $M = 1$, $N = 0$ [cf. Eqs. (28) and (29)] for each \mathbf{q} . The correlation function for $|\Psi(\mathbf{r})|^2$ involves such a single excitation in two separate modes as well as a “double excitation” in one q mode. The former are of order $n_q(n_q - 1)$ in number, whereas the latter are of order n_q (where n_q is the number of q modes). Since n_q is a very large number, we can safely neglect the “double excitations.” Then, we obtain

$$\rho_0^4 C_Q(t) \equiv \langle \Delta \rho_i^2(\mathbf{r}) \Delta \rho_0^2(\mathbf{r}) \rangle = [\rho_0^2 C(t)]^2 \quad (\text{A16})$$

with $C(t)$ given by Eq. (31a). We can then write for the quadratic spectral density $J_Q(\omega)$,

$$J_Q(\omega) = \text{Re} \int \tilde{J}(\omega_1) \tilde{J}(\omega - \omega_1) d\omega_1 \quad (\text{A17})$$

with $\tilde{J}(\omega) = \int_0^\infty C(t) e^{-i\omega t} dt$ [note that $\text{Re} \tilde{J}(\omega) = J(\omega)$ of Eq. (30)]. Equation (A17) is evaluated in Appendix C.

APPENDIX B: CRITICAL DYNAMICS AND SLOW MOTIONS IN ESR

Previously, we suggested criteria for the validity of the motional narrowing approach for spin relaxation due to slow cooperative fluctuations.² This becomes especially relevant in the critical region when there is critical slowing down of the modes. First, we note the important role played by the coherence length ξ . A finite ξ prevents a divergence in the spectral densities $J(\omega)$ as $\omega \rightarrow 0$ as evidenced by Eqs. (31b) and (32b) and previously discussed. There is another physically unrealistic divergence in $J(\omega)$ occurring when $\tau_m \rightarrow \infty$ as the critical point is reached. That is, $J(0)$ given by Eq. (31b) goes as $\tau_m / \xi \propto \xi^{1/2}$ which is diverging near the critical point. However, spectral densities available for spin relaxation do not diverge. Instead, the motional narrowing theory loses its validity and the critical modes no longer provide a mechanism for relaxation. The fluctuations become frozen on the ESR time scale and would lead to static or inhomogeneous line broadening. A sufficient condition for motional narrowing theory in the present context is that the $\hat{T}_2 \ll \tau_m$, where \hat{T}_2 is the contribution to T_2 due to the critical fluctuations. This is perhaps too severe, and it was pointed out previously² that in the model of independent q modes a more detailed analysis could be made if we required for the q th mode that $T_{2,q}^{-1} \sim |H_{1,q}^2| \tau_q \ll \tau_q^{-1}$, where $H_{1,q}$ is the component of $H_1(\Psi)$, which is modulated by the q th mode

of the fluctuations and τ_q^{-1} is given by Eq. (10). This would then be a condition for validity of the motional narrowing theory for the contribution of the q th mode. In the present case we can write

$$|H_{1,q}^2| \sim f^2 \omega_s^2 / \alpha_q, \quad (\text{B1})$$

where f measures the extent of coupling of the probe to the critical modes and ω_s is the magnitude of the typical terms in the spin Hamiltonian. Thus, the crossover mode from those contributing fast to those contributing slow motion should come at

$$1 = |H_{1,q}^2| \tau_q^2 \approx \frac{k_b T}{2AV} \frac{f^2 \omega_s^2 \tau_m^2}{(1 + q^2 \xi^2)^{1+2x}}. \quad (\text{B2})$$

[Note that $|H_{1,q}^2|$ is estimated from the expression for $C_q(t)$ given by Eq. (29b) which shows that it is proportional to α_q^{-1} .] This criterion thus appears to depend upon the sample volume V which does not appear useful or realistic. Instead, if we now recognize this coherence in fluctuations persists only over lengths of the order of ξ , one might expect that $V \sim \xi^3$, i.e., this is the natural volume within which to consider the fluctuations.

A more rigorous analysis of this matter could be performed by using a more complete slow-motional theory. Preliminary results utilizing the partial time-order cumulant (PTOC) method^{26,27} were outlined previously.² A great simplification occurs if we (i) ignore the non-Gaussian features of fluctuations in a complex order parameter Ψ (cf. Appendix A), and (ii) ignore the fact that, for perturbations which do not commute with H_0 , the generalized cumulants which ensue do not exhibit "generalized Gaussian" behavior even if the fluctuations in Ψ did. We will assume instead that the overall process involving the superposition of all the many q modes will approximately satisfy the central limit theorem and thereby appear Gaussian. (This is suggested in part by the vanishing of the higher-order simple cumulants involving cross terms between the different q modes.) In this limit, the line shape is completely determined by just the second cumulant $K_2(t)$. We illustrate with just the secular terms. Thus

$$I(\omega) = \text{Re} \int_0^\infty e^{-i(\omega - \omega_0)t - K_2(t)} dt, \quad (\text{B3})$$

where $I(\omega)$ is the line shape. Now $K_2(t)$ is given by

$$K_2(t) = - \int_0^t dt' \int_0^{t'} dt'' \kappa_2(t', t''). \quad (\text{B4})$$

Here $\kappa_2 = m_2$, the second-order time correlation function for the process. That is,

$$m_2 = \sum_q m_{2,q}, \quad (\text{B5a})$$

$$m_{2,q}(t', t'') = \alpha_q^{-1} e^{-(t' - t'')/\tau_q} f^2 \omega_s^2. \quad (\text{B5b})$$

When we consider the individual q modes, we see via Eq. (B2) that those for which $q^2 \xi^2 \ll 1$ do approach the slow-motional condition as $(T - T_c)^{-4/3}$, but those for which $q^2 \xi^2 \gg 1$ cannot be brought to the slow-motional condition [since the right-hand side of Eq. (B2) goes as $(T - T_c)^2$].

Furthermore, the condition $q^2 \xi^2 \ll 1$ is fulfilled by fewer q modes as ξ diverges. Clearly, this problem of fast vs slow motion is a complex one deserving of further study.

If we consider the rigid limit in the above-noted Gaussian approximation, we have

$$\begin{aligned} \kappa_2(t) = & - \sum_q \{ \alpha_q^{-1} \tau_q^2 [t/\tau_q - 1 + \exp(-t/\tau_q)] \} f^2 \omega_s^2 \\ & - \frac{V f^2 \omega_s^2}{(2\pi)^3} \int d\mathbf{q} \alpha_q^{-1} \tau_q^2 [t/\tau_q - 1 + \exp(-t/\tau_q)]. \end{aligned} \quad (\text{B6})$$

The fast-motional limit applies when the first term in the square brackets is dominant for times of interest.²⁸ By analogy with simple single mode cases,² we may specify this condition as

$$\frac{V f^2 \omega_s^2}{(2\pi)^3} \int_0^{q_c} d\mathbf{q} \alpha_q^{-1} \tau_q^2 \ll 1 \quad (\text{B7})$$

(i.e., the second term in the square brackets is small). This yields (letting $x = 1$ for convenience)

$$\frac{k_b T}{2A} \frac{f^2 \omega_s^2 \tau_m^2}{(32\pi)} \xi^{-3} = M k_b T f^2 \omega_s^2 \tau_m^2 / 32\pi \xi \ll 1 \quad (\text{B8})$$

(which is valid for $q_c \gg \xi^{-1}$). The crossover to slow motion should come when this quantity equals unity. This condition applies to the overall line shape, i.e., the resultant of all the q modes. A breakdown into the effects of the individual q modes could, in principle, be made by retaining the sum over \mathbf{q} in $K_2(t)$ [cf. Eq. (B6)] and by replacing the sum which would ensue in the exponent of Eq. (B3) by a product of exponentials. This is important for a quantitative theory, because the higher q modes could still contribute to motional narrowing, while the lower q modes are "slow motional."

If we now compare Eq. (B2) (with $x = 1$) with Eq. (B8), then we see that the criterion of Eq. (B2) would become equivalent, if we let $q^2 \rightarrow \xi^{-2}$ in Eq. (B2) and then let V in Eq. (B2) be a sphere of radius $r = 3^{1/3} \xi$. This is consistent with our notion that the relevant volume is of order ξ^3 (not the total sample volume as *incorrectly* utilized in Ref. 2). It also suggests that a typical or "mean" q mode is that for which $q^2 = \xi^{-2}$.

Now when we recall $\tau_m^2 \propto \xi^3$, we see that the left-hand side of Eq. (B8) diverges as $\xi^2 \propto (T - T_c)^{-4/3}$. Thus, a slow-motional condition should be achieved as one approaches T_c close enough. In the experiments reported in paper II, the smallest values of $(T - T_c)/T_c$ studied were 3×10^{-4} , which for the values estimated there could imply incipient slow-motional behavior, but the uncertainty in magnitude of key parameters renders this matter uncertain.

Now in the rigid limit one has in this Gaussian approximation

$$K_2(t) \rightarrow - \frac{t^2}{2} \sum_q \alpha_q^{-1} f^2 \omega_s^2 = - \frac{t^2}{2} \Delta^2, \quad (\text{B9})$$

where

$$\Delta^2 \equiv f^2 \omega_s^2 k_b T q_c / 2\pi^2 (2A) \xi^2 = f^2 \omega_s^2 M k_b T q_c / 2\pi^2$$

(and it was assumed that $q_c^2 \gg \xi^{-2}$) corresponding to Gaus-

sian inhomogeneous broadening of rms width Δ , which would only very weakly approach zero as $M \propto \xi^{-\eta/2}$ where $\eta = 0.04$.

Note that in the above discussion we have neglected the effect of finite diffusion. Our results in Sec. II lead to the suggestion that we replace τ_m in the present expressions by $\tau'_m = z\tau_m$ [cf. Eqs. (33)].

APPENDIX C: EFFECTS OF ANISOTROPY IN THE MEDIUM

1. Fluctuations in the smectic order parameter

If we include anisotropy in $\xi \rightarrow \xi_{\parallel}$ and ξ_{\perp} , and in $D \rightarrow D_{\parallel}$ and D_{\perp} , then $J(\omega)$ [cf. Eqs. (29)–(30)] becomes [where we let $x = 1$ in Eq. (10) for simplicity]

$$J(\omega) = \frac{k_b T}{8A(2\pi)^3} \text{Re} \int_0^{\alpha_c} d^3q \times [1 + q_{\perp}^2 \xi_{\perp}^2 + (q_{\parallel} - q_s)^2 \xi_{\parallel}^2]^{-1} \times \{i\omega + \tau_m^{-1} \times [1 + q_{\perp}^2 (\xi_{\perp}^2 + D_{\perp} \tau_m) + (q_{\parallel} - q_s)^2 \xi_{\parallel}^2 + q_{\parallel}^2 D_{\parallel} \tau_m]\}^{-1}. \tag{C1}$$

Now let

$$P_{\perp}^2 = q_{\perp}^2 (\xi_{\perp}^2 + D_{\perp} \tau_m) \tag{C2a}$$

and

$$P_{\parallel}^2 = (q_{\parallel} - q_s)^2 (\xi_{\parallel}^2 + D_{\parallel} \tau_m). \tag{C2b}$$

Then, if we let $q_c \rightarrow \infty$ and $q_s = 0$,

$$J(\omega) = \frac{k_b T}{8A(2\pi)^3} [(\xi_{\perp}^2 + D_{\perp} \tau_m)(\xi_{\parallel}^2 + D_{\parallel} \tau_m)^{-1/2}]^{-1} \times \text{Re} \int_0^{\infty} d^3P \left(1 + \frac{P_{\perp}^2}{1 + D_{\perp} \tau_m \xi_{\perp}^{-2}} + \frac{P_{\parallel}^2}{1 + D_{\parallel} \tau_m \xi_{\parallel}^{-2}}\right)^{-1} \times [i\omega + \tau_m^{-1}(1 + P^2)]^{-1}. \tag{C3}$$

Now if $\tau_m \sim \xi^{3/2}$ it then follows that $D_{\perp} \tau_m \xi_{\perp}^{-2}$ and $D_{\parallel} \tau_m \xi_{\parallel}^{-2}$ go to zero as $\xi^{-1/2}$. If we ignore these terms, then we may write

$$J(\omega) \sim \frac{k_b T \tau_m}{8A(2\pi)^3 \xi_{\perp}^2 \xi_{\parallel}} \int_0^{\infty} d^3P [\omega^2 \tau_m^2 + (1 + P^2)^2]^{-1}. \tag{C4}$$

We may let $A\xi_{\perp}^2 = (2M_T)^{-1}$ and consider $J(0)$:

$$J(0) \sim \frac{k_b T M_T \tau_m}{4(2\pi)^3 \xi_{\parallel}} \int_0^{\infty} d^3P (1 + P^2)^{-2} \propto \xi^{1/2} M_T \propto \xi^{0.46} \propto (T - T_c)^{-0.31}, \tag{C5}$$

which may be compared with Eq. (31b). A more general analysis of anisotropy of the medium appears in paper II.

We now consider the $J(\omega)$ emanating from the quadratic correlation terms in $\Delta\rho(\mathbf{r})$ [cf. Eq. (1)]. We obtain from Eq. (A17)

$$J_Q(\omega) = \left[\frac{k_b T}{8A(2\pi)^3}\right]^2 \text{Re} \int d\mathbf{q}_1 \int d\mathbf{q}_2 [(1 + q_{1,\perp}^2 \xi_{\perp}^2 + q_{1,\parallel}^2 \xi_{\parallel}^2)(1 + q_{2,\perp}^2 \xi_{\perp}^2 + q_{2,\parallel}^2 \xi_{\parallel}^2)]^{-1} \times [i\omega + \tau_m^{-1}(\xi_{\perp}^2 + D_{\perp} \tau_m)(q_1^2 + q_2^2) + (\xi_{\parallel}^2 + D_{\parallel} \tau_m)(q_1^2 + q_2^2)]^{-1}. \tag{C6}$$

The same substitutions [i.e., Eqs. (C2)] lead to

$$J_Q(\omega) = \left[\frac{k_b T}{8A(2\pi)^3(\xi_{\perp}^2 + D_{\perp} \tau_m)(\xi_{\parallel}^2 + D_{\parallel} \tau_m)^{1/2}}\right]^2 \tau_m \times \int d^3P_1 \int d^3P_2 \left(1 + \frac{P_{1,\perp}^2}{1 + D_{\perp} \tau_m \xi_{\perp}^{-2}} + \frac{P_{1,\parallel}^2}{1 + D_{\parallel} \tau_m / \xi_{\parallel}^2}\right)^{-1} \times \left(1 + \frac{P_{2,\perp}^2}{1 + D_{\perp} \tau_m \xi_{\perp}^{-2}} + \frac{P_{2,\parallel}^2}{1 + D_{\parallel} \tau_m / \xi_{\parallel}^2}\right)^{-1} \frac{1 + P_1^2 + P_2^2}{\omega^2 \tau_m^2 + (1 + P_1^2 + P_2^2)}. \tag{C7}$$

Thus as $\xi \rightarrow \infty$, the zero-frequency spectral density $J_Q(0)$ goes as

$$J_Q(0) \sim \frac{(k_b T)}{(2\pi)^6} \frac{T_m}{(8A)^2 \xi_{\perp}^4 \xi_{\parallel}^2} \times \int d^3P_1 \int d^3P_2 (1 + P_1^2)^{-1} (1 + P_2^2)^{-1} \times (1 + P_1^2 + P_2^2)^{-1}. \tag{C8}$$

Then, we find that

$$J_Q(0) \propto M_T^2 \tau_m / \xi_{\parallel}^2 \propto M_T^2 \xi^{-1/2} \propto (T - T_c)^{1.16/3}. \tag{C9}$$

Thus $J_Q(0)$ goes to zero as the critical point is reached, and will not be important. We may, in a similar fashion, consider correlations of the higher power terms in the expansion of Eq. (1). They might be expected to go to zero more rapidly if we systematically ignore all but “single-excitation” terms (cf. Appendix A). However, this will no longer be valid for the general M th-order term (i.e., the ratio of number of terms contributing more than single excitations to the M -tuple sum vs the number contributing to single excitations go as $[(n_q)^M (n_q - M)! / n_q! - 1]$).

2. Fluctuations in nematic director

We now consider Brochard's proposed mechanism for nuclear-spin relaxation.⁷ It is based upon fluctuations in the nematic director, which become suppressed as the force constants for twist and bend K_2 and K_3 approach infinity near the smectic phase transition due to coupling between the nematic director and the smectic order parameter. One has that K_2 and $K_3 \propto \xi$, while γ_e is the twist viscosity $\propto \xi^{-1/2}$ (but see Mulvaney and Swift²⁹).

One then employs the expressions for spin relaxation due to director fluctuations. These are two normal-mode components of $\delta_{\mathbf{a}}$ in the x - y plane with mean-square fluctuations given by

$$\langle |n_{1,q}|^2 \rangle = k_b T / (K_1 q_1^2 + K_3 q_{\parallel}^2), \quad (\text{C10a})$$

$$\langle |n_{2,q}|^2 \rangle = k_b T / (K_2 q_1^2 + K_3 q_{\parallel}^2). \quad (\text{C10b})$$

We now label the spectral densities from fluctuations in these components: $J_1(\omega)$ and $J_2(\omega)$, respectively. Then,

$$J_1(\omega) = \frac{k_b T}{(2\pi)^3} \text{Re} \int d\mathbf{q} (K_3 q_{\parallel}^2 + K_1 q_1^2)^{-1} \times [\omega + (D_{\parallel} + K_3/\gamma_e) q_{\parallel}^2 + (D_1 + K_1/\gamma_e) q_1^2]^{-1}, \quad (\text{C11})$$

while $J_2(\omega)$ is obtained from $J_1(\omega)$ by replacing $K_1 \rightarrow K_2$. Now, we let

$$P_{\perp}^2 = q_1^2 (D_1 + K_1/\gamma_e), \quad (\text{C12a})$$

$$P_{\parallel}^2 = q_{\parallel}^2 (D_{\parallel} + K_3/\gamma_e). \quad (\text{C12b})$$

(Note that here P_{\perp}^2 and P_{\parallel}^2 are in units of s^{-1} .) Then,

$$J_1(\omega) = \frac{k_b T}{\gamma_e (2\pi)^3} [(D_{\parallel} + K_3/\gamma_e)(D_1 + K_1/\gamma_e)]^{-1} \times \int \frac{d^3 P}{\omega^2 + P^4} [(1 + D_{\parallel} \gamma_e / K_3)^{-1} \cos^2 \theta + (1 + D_1 \gamma_e / K_1)^{-1} \sin^2 \theta]^{-1}, \quad (\text{C13})$$

where $\cos^2 \theta = P_{\parallel}^2 / P^2$ and $\sin^2 \theta = P_{\perp}^2 / P^2$.

Now, as $\xi \rightarrow \infty$, $D_{\parallel} \gamma_e / K_3 \rightarrow 0$, but $D_1 \gamma_e / K_1 \propto \xi^{1/2}$, so

$$J_1(\omega) \sim \frac{k_b T}{(2\pi)^3 (K_3 \gamma_e)^{1/2} D_1} \int \frac{d^3 P}{(\omega^2 + P^4) \cos^2 \theta} \propto \xi^{-3/4} \propto (T - T_c)^{1/2}. \quad (\text{C14})$$

Thus, as Brochard points out, this spectral density goes to zero. It does not diverge. Similarly,

$$J_2(\omega) = \frac{k_b T}{\gamma_e (2\pi)^3} [(D_{\parallel} + K_3/\gamma_e)^{1/2} (D_1 + K_2/\gamma_e)]^{-1} \times \int \frac{d^3 P}{\omega^2 + P^4} [(1 + D_{\parallel} \gamma_e / K_3)^{-1} \cos^2 \theta + (1 + D_1 \gamma_e / K_2)^{-1} \sin^2 \theta]^{-1} \cong \frac{k_b T \gamma_e^{1/2}}{(2\pi)^3 (K_2^2 K_3)^{1/2}} \int \frac{d^3 P}{\omega^2 + P^4} \propto \xi^{-5/4} \propto (T - T_c)^{5/6}, \quad (\text{C15})$$

so it goes to zero faster than $J_1(\omega)$. (Brochard gives this exponent incorrectly.) (Mulvaney and Swift,²⁷ in their reanalysis of NMR relaxation based on a more modern treatment of critical exponents, ignore the role of molecular diffusion. Nevertheless, they also predict that the spectral densities will go to zero.) Furthermore, from the spin selection rules associated with the mechanism for director fluctuations,² this mechanism cannot contribute to secular relaxation (i.e., terms with no spin flips) that are needed to explain our experimental results.^{3,14}

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¹⁹A more general approach, which more explicitly includes the manner by which density fluctuations modulate the spin relaxation, is to include the well-known fact that the molecular potential U is also a function of molecular orientation, Ω . As smectic layers begin to form, there is a coupling between orientational ordering and position in the smectic layer, which may be represented by a cross term in U [cf. G. Moro and P. L. Nordio, *J. Phys. Chem.* **89**, 997 (1985); J. H. Freed, in *Rotational Dynamics of Small and Macromolecules*, edited by T. Dorfmueller and R. Pecora, Vol. 293 in *Lecture Notes in Physics* (Springer-Verlag, Berlin, 1987)]. Evidence for such a cross term deep in the smectic was recently provided by the ESR studies of J. Gorcester, S. Rananavare, and J. H. Freed [*J. Chem. Phys.* **90**, 5764 (1989)]. Thus, near the phase transition, we may write to lowest order:

$$U[\Delta\rho(\mathbf{r}), \Omega] \approx u_1 \Delta\rho(\mathbf{r}) + \lambda_2 \mathcal{D}_{00}^2(\Omega) + w \Delta\rho(\mathbf{r}) \mathcal{D}_{00}^2(\Omega) + \dots$$

One must then solve for the combined translational and rotational diffusion of the probe molecule subject to this type of potential in order to obtain fluctuations in $S \equiv P_{\text{es}}(\Omega) \mathcal{D}_{00}^2(\Omega) d\Omega$ induced by fluctuations in $\Delta\rho(\mathbf{r})$ and/or fluctuations in the rotational relaxation of the probe from this same source. Our use of Eq. (1) and just Eq. (3) simplifies the analysis at the expense of introducing some imprecision into the mechanism whereby the spin relaxation is affected by fluctuations in smectic order.

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case, since the propagating mode known as second sound only becomes significant deep in the smectic phase [cf. L. Ricard and J. Prost, *J. Phys.* **42**, 861 (1981)], but goes to zero near T_{NS_s} . In fact, Brochard [Ref. 8(b)] made clear that second sound does *not* affect the relaxation in fluctuations of smectic order parameter $\Psi(r,t)$ close to T_{NS_s} , since this is a purely dissipative viscoelastic mode with $\tau_m = \bar{\eta}/B$, where $\bar{\eta}$ is the renormalized viscosity and B is the rigidity coefficient for compression of the smectic layers. Finally, Jähnig [*J. Phys.* **36**, 315 (1975)] has emphasized that there will be a symmetry of fluctuation effects about T_{NS_s} , so we can safely assume that the Jähnig–Brochard theory for $T > T_{NS_s}$ should also apply for $T < T_{NS_s}$, except for the fact that below T_{NS_s} , Ψ will have a nonequilibrium value, Ψ_0 (Ref. 7).

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