MOLECULAR DYNAMICS AT THE NEMATIC TO SMECTIC A PHASE TRANSITION: AN ESR STUDY

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Received 16 May 1984

In an electron-spin-relaxation study of a spin probe dissolved in a liquid crystal, the linewidth parameters are observed to diverge in the nematic phase with critical exponent close to 1/3 as the nematic–smectic A transition is approached. This is interpreted in terms of a model wherein pre-transitional smectic fluctuations modulate the spin-relaxation parameters of the probe.

While the electron-spin relaxation of spin probes dissolved in liquid-crystalline solvents is reasonably well understood at the isotropic–nematic phase transition [1,2], the nematic–smectic transition has been virtually unexplored by equivalent studies (including NMR [3]), despite the current great interest in this transition [4–6]. In general, spin-relaxation studies of liquid-crystalline phase transitions with their (nearly)-second-order nature can shed light on the subtle molecular features which characterize these transitions. Since spin-relaxation phenomena typically show critical types of divergences at such transitions, there is also the question of how the molecular dynamics couples to the hydrodynamic modes. Given the extensive study of the collective variables and their critical exponents [4–6], clues to the nature of this coupling can be obtained from observing the critical exponents characterizing the spin relaxation. This will also help focus on the molecular motions that are being probed by the spin relaxation. Ultimately, once these matters are clarified, one can ask to what extent the studies on spin relaxation with their inherent complexities can reflect back upon the general features of the phase transition under investigation.

In this Letter we report on observations we have made in an electron-spin-relaxation study of the nematic–smectic phase transition, and we propose a model to interpret them.

The study we report on was performed with the spin-probe PD-Tempone (PDT) dissolved in the liquid crystal N-(*p*-butoxybenzylidene)-*p*-*n*-hexylaniline (40,6) to yield solutions of 4×10^{-4} M concentration [7]. Degassed samples were contained in a small glass capillary to form a cylindrical sample of dimensions 20 mm in length and 0.9 mm in diameter. An X-band ESR spectrometer designed for millikelvin temperature control was utilized [8]. It provides temperature stability of ±2–4 mK for a typical set of measurements taken over a period of ≈1 h. The ESR spectra obtained in this work were motionally narrowed. This permits a standard linewidth analysis in terms of the coefficients B and C representing the expansion of the linewidth δ as a function of the ^{14}N nuclear spin quantum number M_I: $\delta = A + BM_I + CM_I^2$ [1,2,7].

Critical-type divergences were observed on both sides of the I–N transition as well as on the nematic side of the N–S_A transition for all the hyperfine lines. The data required significant non-linear least-squares fitting to extract the critical contribution to the linewidths at each transition. The critical divergences in linewidth are illustrated in figs. 1 and 2 while the results of the non-linear least-squares fits appear in table 1. The I–N phase transition is characterized (on either side) by spin-relaxation parameters which diverge with exponent close to 1/2 as is consistent with a Landau–de Gennes mean-field theory of fluctua-

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0 009-2614/84/$ 03.00 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division)

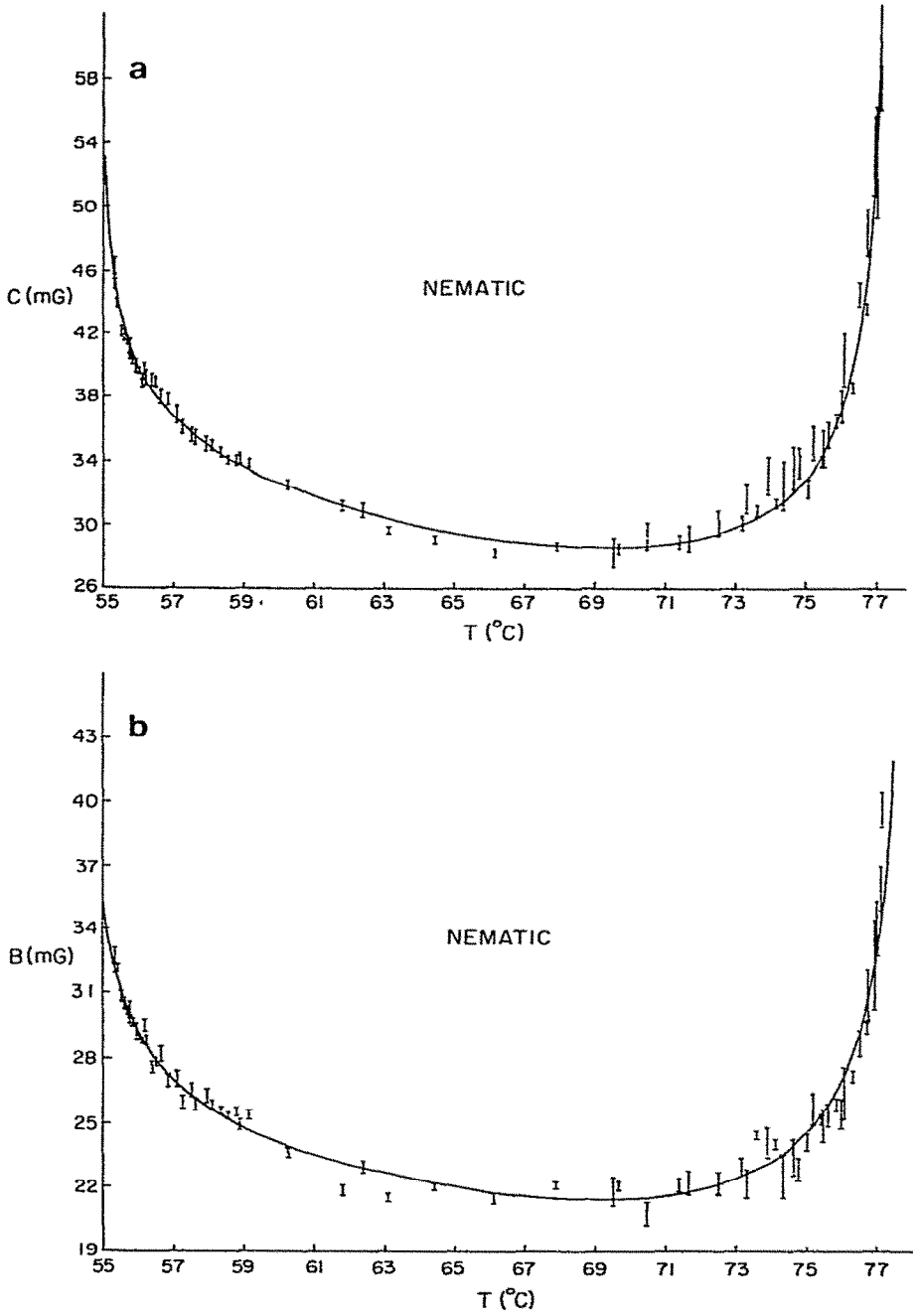

Fig. 1. Linewidth parameters C (a) and B (b) versus temperature in the nematic phase for PD-Tempone in 40,6. The data are shown with their uncertainty (i.e. one standard deviation). The solid curve is the least-squares fit based on the parameters in table 1.

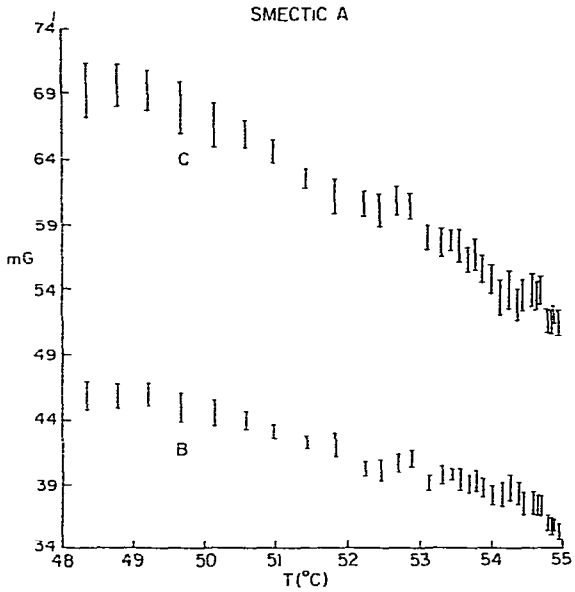

Fig. 2. Linewidth parameters B and C versus temperature in the smectic A phase for PD-Tempone in 40,6.

tions in the orientational order parameter [1]. This results in a slowly-fluctuating orientational potential at the site of the probe molecule, which is able to modulate the rotational reorientation of the probe, thereby leading to the observed critical-type of effect on the spin relaxation [1,2]. On the other hand, the critical exponent observed at the N–S_A phase is close to 1/3. While the weak first-order I–N phase transition is generally well-characterized by mean-field theory, this is not so for the N–S_A transition, which is most likely second order for 40,6 [6] and to which scaling laws analogous to the λ transition in He have been applied [9,10]. In the dynamic scaling approach of Brochard [10] and of Jähnig and Brochard [11] the coherence length ξ characterizing fluctuations in the smectic order parameter

Table 1
Phase transition results for PD-Tempone in 40,6

Transition	Parameter	B analysis	C analysis
Nematic phase [a,b]: $B, C = k_1(T-T_c)^{\gamma_1} + k_2(T^*-T)^{\gamma_2} + k_3 \exp[k_4/(T+273.15)]$			
N–S_A	k_1 (mG)	12.8 ± 2.0	15.2 ± 2.3
	T_c (°C)	54.8 ± 0.2	54.8 ± 0.1
	γ_1	−1/3 (fixed)	−0.328 ± 0.072
N–I	k_2 (mG)	20.5 ± 1.0	23.7 ± 1.1
	T^* (°C)	78.0 ± 0.1	77.44 ± 0.08
	γ_2	−1/2 (fixed)	−0.475 ± 0.061
background width	k_3 (mG)	(1.01 ± 0.15) × 10^{-3}	(1.02 ± 0.11) × 10^{-3}
	k_4 (K)	3120 ± 50	3250 ± 35
Isotropic phase [c]: $B, C = k_2(T-T^*)^{\gamma_2} + k_3 \exp[k_4/(T+273.15)]$			
I–N	k_2 (mG)	2.94 ± 0.31	16.8 ± 1.5
	T^* (°C)	77.2 ± 0.1	76.9 ± 0.1
	γ_2	−0.50 ± 0.11	−0.55 ± 0.07
background width	k_3 (mG)	(1.54 ± 0.54) × 10^{-3}	(1.25 ± 0.79) × 10^{-3}
	k_4 (K)	3400 ± 130	3420 ± 240

a) The data in the nematic phase were fit to this equation by non-linear least squares [8]. Full convergence was obtained for the C linewidth analysis, but not for the B linewidth analysis in this phase. By fixing the critical exponents for B as those from the C linewidth analysis, overall consistency could be demonstrated by the good correspondence between the other parameters.

b) The term $k_1(T-T_c)^{\gamma_1}$ is the critical contribution near the N–S_A transition, while $k_2(T-T^*)^{\gamma_2}$ is the critical contribution near the I–N transition, and $k_3 \exp[k_4/(T+273.15)]$ gives the background linewidth due to rotational reorientation which typically may be fit to an Arrhenius temperature dependence.

c) The data in the isotropic phase were fit to this equation by non-linear least squares [8]. Full convergence was obtained for both the B and C linewidth analyses. The term $k_2(T-T^*)^{\gamma_2}$ is the critical contribution near the I–N transition, and $k_3 \exp[k_4/(T+273.15)]$ gives the background linewidth.

$\Psi(r, t)$, which is complex, is predicted to diverge as $(T - T_c)^{-0.66}$. While the true story is more complicated, involving separate critical exponents for $\xi_{\parallel}$ and $\xi_{\perp}$ (the coherence lengths parallel and perpendicular, respectively, to the nematic director), and these exponents appear to vary from one liquid crystal to another [4–6], we shall use as our point of reference, the Jähnig–Brochard theory for the present work.

Brochard [10] had indeed predicted critical effects at the N–S_A transition for NMR relaxation. Her model (as well as a more recent discussion [12]) involves the fact that as the transition is approached, the Frank elastic constants for twist and bend deformations K_2 and K_3 diverge as $(T - T_c)^{-0.66}$. Thus director fluctuations and their resultant spin-relaxation effects are suppressed as the transition is approached. However, director fluctuations have not been found to make a significant contribution to the ESR relaxation in the nematic phase [2,13], and also the Brochard mechanism would predict a reduction in the linewidths as the N–S_A transition is approached. Instead they are all observed to diverge. Furthermore, the spin selection rules for the Brochard mechanism are also inconsistent with our observations. (That is, for this mechanism, the A term should decrease, the B term should be unaffected, while the C term should increase, but not as rapidly as the A term decreases. We observed A, B, and C to increase.) Thus we conclude that this mechanism does not explain our observations.

Instead, we take a different approach motivated by our past observation that the PDT probe appears to be expelled from the aromatic core as the temperature is lowered in the smectic phase [7]. This is evidenced by (i) a decrease in ordering of PDT with decrease in T in this phase, (ii) the significantly lower activation energy for reorientation of PDT in the smectic versus nematic and isotropic phases, and also (iii) the decrease in isotropic hf splitting with decrease in T consistent with the probe moving into the region of the non-polar hydrocarbon chains [7].

Based on the above facts, we propose the following model. The probe has a preference to be located in the lower-density regions of the smectic layer, i.e. the alkyl chain region. As the smectic phase is approached from above, and smectic layering forms as a pre-transitional phenomenon (i.e. cybotactic clusters), there is "expulsion" of the probe to the lower-density regions of the transitory smectic layer. Molecular parameters which affect spin relaxation (e.g. the nematic ordering parameter S_p and/or τ_R, the rotational correlation time) are affected by this "expulsion" effect. The onset of smectic layers near the transition is described by density fluctuations $\rho(r, t)$ which also affects the translational motion of the probe. Since the critical fluctuations in $\rho(r, t)$ occur on a much longer time-scale than probe dynamics, there is a time-scale separation of the two types of motions which simplifies the analysis. Thus, as cybotactic clusters form and breaks up in different regions, molecular dynamics and therefore the spin relaxation of the probe is modulated.

Our formal approach is as follows. First we expand the relevant relaxation parameter Q(= e.g. S_p or τ_R) as a Taylor series in the deviation of the density from its mean value ρ_0, i.e. in $\Delta\rho(r, t) \equiv \rho(r, t) - \rho_0$:

$$Q(r, t) = Q_0 + Q_1 \Delta\rho(r_B, t) + Q_2 [\Delta\rho(r, t)]^2 + \ldots, \quad (1)$$

where the subscript B refers to the location of the probe. The translational diffusion of the probe is taken to obey a Smoluchowski equation with a time-dependent potential [2]:

$$\partial P(r_B, t)/\partial t = -\nabla \cdot \mathbf{D} \cdot \{\nabla + [\nabla U(r_B, t)]/kT\} P(r_B, t). \quad (2)$$

In eq. (2), $P(r_B, t)$ is the probability density of finding the probe at r_B at time t, $\mathbf{D}$ is the translational diffusion tensor with components $D_{\parallel}$ and $D_{\perp}$, while the potential of mean force on the probe is a functional of the density fluctuations, i.e.

$$U(r_B, t) = U[\Delta\rho(r_B, t)]. \quad (3)$$

Now $\Delta\rho(r)$ is related to the complex order parameter $\Psi(r)$ in the usual manner [10 11]:

$$\Delta\rho(r) = 2^{-1/2} \rho_0 \, \mathrm{Re}[\Psi(r) \exp(\mathrm{i} q_s z)]$$

$$= 2^{-1/2} \rho_0 \, |\Psi(r)| \, \mathrm{Re}(\exp\{\mathrm{i} q_s [z - u(r)]\}). \quad (4)$$

Here $q_s = 2\pi/d$, where d is the smectic layer spacing, and the phase, $q_s u(r)$ of $\Psi(r)$ locates the smectic layer's density maxima and minima in each part of the sample. If we follow dynamic scaling according to Jähnig and Brochard [9,10], we obtain for the qth Fourier component of $\Psi(r)$ the time correlation function:

$$\langle \Psi^*(q, t) \Psi(q, 0) \rangle = \langle |\Psi_q|^2 \rangle \exp(-\Gamma_q t), \quad (5)$$

where the mean-square fluctuation of the qth mode is:

$$\langle|\Psi_q|^2\rangle = (k_B T/2A)[(1+q_\perp^2\xi_\perp^2 + q_\parallel^2\xi_\parallel^2)V]^{-1}. \quad (6)$$

Here $q_\parallel$ and $q_\perp$ are the components of q parallel and perpendicular (to the nematic director), V is the sample volume, and A is the coefficient in the term quadratic in $\Psi(r)$ in the Landau expansion of the smectic free energy. (A goes to zero almost as ξ^{-2}.) The damping Γ_q of the qth mode is given by:

$$\Gamma_q^{-1} = \tau_m/(1+q_\perp^2\xi_\perp^2 + q_\parallel^2\xi_\parallel^2)^x, \quad (7)$$

with τ_m a characteristic relaxation time for the cybotactic clusters (it may also be written as $\tau_m = \gamma_3/2A$ where γ_3 is the viscosity coefficient for motion of the smectic planes relative to the background liquid [14, 15]) and $x = 3/4$. The relaxation time τ_m is expected to diverge as $\xi^{3/2} \propto (T-T_c)^{-1}$.

In the spirit of a Landau expansion we consider only the lowest-order terms in $\Delta\rho(r_B)$ to represent the time-dependent fluctuations in Q. That is:

$$\langle\Delta Q(r_B, t)\,\Delta Q(r_B, 0)\rangle = Q_1^2 C(t) + \text{higher-order terms}, \quad (8)$$

where

$$C(t) \equiv \langle\Delta\rho(r_B, t)\,\Delta\rho(r_B, 0)\rangle/\rho_0^2. \quad (9)$$

The method of approach for calculating $C(t)$ including the critical hydrodynamics of the phase transition and the translational diffusion of the probe is analogous to methods previously developed [2]. (In our present analysis we do not invoke the decoupling approximation between the real and the imaginary part of the order parameter used by Jähnig and Brochard. Instead we regard $\Psi(q, t)$ as obeying a "hindered diffusion in the complex plane". The results are similar in lowest order.) Since the results are, in general, quite complicated we consider two simplifying special cases below.

We first let $q_s \to 0$, which may at first appear unphysical, but we discuss the matter further below. We also ignore any anisotropies, so that $\xi_\parallel = \xi_\perp = \xi$ and $D_\parallel = D_\perp = D$ and we let $x = 1$ in eq. (7). We then obtain for the spectral density, $J(\omega) \equiv \frac{1}{4}\,\mathrm{Re}\int_0^\infty C(t)\,e^{-i\omega t}dt$, the result:

$$J(\omega) = (Mk_B T/4\pi)\,\xi \times \{D[1+(\tfrac{1}{2}z)^{1/2}((1+\omega^2\tau_m^2)^{1/2}+1)^{1/2}] + 2^{-1/2}\,\omega\xi^2 z^{1/2}((1+\omega^2\tau_m^2)^{1/2}-1)^{1/2}\} \times (\omega^2\xi^4 + D^2)^{-1}, \quad (10)$$

where $z \equiv (1 + D\tau_m/\xi^2)^{-1}$ measures the relative importance of translational diffusion over the coherence length ξ versus relaxation of the order parameter in providing averaging of the fluctuations in Q. Also, $M^{-1} = (2A\xi^2)$ exhibits only a very weak divergence (i.e. $M^{-1} \propto \xi^\eta$, $\eta = 0.04$) that we ignore below. The dominant contributions to the ESR linewidths should be from terms involving $J(\omega) \approx J(0)$ [1,2] for which eq. (10) becomes:

$$J(0) = (Mk_B T/8\pi)\,(zT_m/\xi)\,(1+z^{1/2})^{-1} \quad (11a)$$

$$\xrightarrow{z \approx 1} (Mk_B T/16\pi)\,(\tau_m/\xi) \propto \xi^{1/2} \propto (T-T_c)^{-1/3} \quad (11b)$$

$$\xrightarrow{z \ll 1} (Mk_B T/8\pi D)\,\xi \propto \xi \propto (T-T_c)^{-2/3}. \quad (11c)$$

Here $z \approx 1$ corresponds to relaxation dominated by director fluctuations, while $z \ll 1$ corresponds to relaxation dominated by molecular translational diffusion. The limiting form for $z \approx 1$ predicts the experimentally observed critical divergence.

In the second case we keep $q_s = 2\pi/d$ but let $D_\parallel\tau_m/\xi_\parallel^2$ and $D_\perp\tau_m/\xi_\perp^2$ both approach zero as T_c is approached. (They do go to zero as $\xi^{-1/2}$.) We also introduce a cut-off $q_c \approx q_s$ but let $q_s\xi_\parallel \to \infty$. (In the previous case we let $q_s \to \infty$.) Then for $J(0)$ we obtain

$$J(0) \approx \frac{Mk_B T}{16\pi}\,\frac{\tau_m}{\xi}\,\frac{(1+c)^{1/2}-1}{c}. \quad (12)$$

Here $c \equiv q_s^2 D_\parallel \tau_m$ measures the relative importance of averaging out the effects of density fluctuations $\Delta\rho(r)$ in a *single* smectic-like layer through diffusion of the probe in the direction normal to the layer versus the relaxation of the smectic layers. As $c \to 0$, corresponding to probe diffusion being unimportant, one obtains essentially the result of eq. (11b). For $c \gg 1$, $J(0) \propto \tau_m^{1/2}/\xi_\parallel \propto \xi^{-1/4}$ and it does *not* diverge, but rather goes to zero.

Based upon measurements of $\xi_\parallel$ [6] and D [16,17] we estimate $\xi_\parallel \approx 10^{-5}$ cm for $T - T_c = 0.1$ K and $D \approx 10^{-6}$ cm^2/s. But τ_m is less well established [18]. Using the theoretical relation between τ_m and the critical contribution to the twist viscosity [11,14] as well as experimental estimates of the latter [19] we estimate $\tau_m \approx 10^{-5}-10^{-6}$ s at $T - T_c = 0.1°$C. Thus $D_\parallel\tau_m/\xi_\parallel^2 \approx 10^{-2}-10^{-1}$ (for $T - T_c \approx 0.1°$C), while $D_\parallel\tau_m q_s^2 \approx 10-10^2$. Thus, while it may be reasonable to ignore the averaging effects of translational diffusion over the distance of $\xi_\parallel$, this is questionable for diffusional

averaging over a single smectic layer of thickness d. (Note, however, that $\xi_\perp$ appears to be about an order of magnitude shorter than $\xi_\parallel$, i.e. $\approx$200 Å when $T - T_c \approx 0.1$°C for the related liquid crystal 40,7 with a critical exponent $\nu_\perp = 0.65$ [6].)

However, the lowest-order model, i.e. eq. (8), implicity ignores the potential of mean force $U(r_B, t)$ in eq. (2). If U is a very sensitive functional of $\Delta\rho(r)$ (cf. eq. (3)), then as $\Delta\rho(r)$ diverges as the critical point is reached, eq. (2) would predict virtually no diffusion parallel to the normal to the smectic phases in the cybotactic clusters. Instead, the probe would reside entirely in the alkyl chain regions in such clusters, i.e. the "expulsion effect" referred to above. Thus, the modulation of the parameter Q would be primarily determined by the formation and break-up of the cybotactic clusters, with the probe rapidly adjusting its location within the layers accordingly. This effect would be measured by the correlation function: $\langle\Psi(r_B,t)\Psi(r_B,0)\rangle$ (instead of eqs. (4) and (9)) for which eqs. (10) and (11) constitute and appropriate solution, while eq. (11b) exhibits the observed critical divergence. We suggest this model as a possible interpretation of the experimental result.

One further comment: the lack of a critical divergence on the smectic side of the N–S_A transition (cf. fig. 2) would have to be explained in terms of a non-negligible Ψ_0, i.e. a non-zero equilibrium value for the smectic order parameter occurring near enough to T_c that the "expulsion effect" is already significant. That is, $U[\Delta\rho(r_B)]$ is sufficiently large that the probe is already primarily in the alkyl chain region, so further fluctuations are not very important. This is consistent with the observation (cf. figs. 1 and 2) that the smectic values of the linewidths (near T_c) are "plateau values", to which those of the nematic appear to approach‡.

‡ There is an apparent analogy between these observations on the molecular level and the divergence in the macroscopic viscosity η_1 for flow parallel to the nematic director. The latter also diverges above T_c with a critical exponent close to 1/3, while just below T_c it increases very rapidly leading to near rigidity in the parallel direction [19]. However, it is generally found that the microviscosities affecting molecular motion do not exhibit the critical contributions to the macroscopic viscosities [16,20].

We plan, in future work, to test for the universality of this N–S_A critical exponent, especially since preliminary evidence on another system [16] seems to indicate this, and also to develop further details of the model.

We wish to thank Dr. Wu-Jui Lin for his extensive help during the early stages of this work and Dr. V.S.S. Sastry and Mr. Akbar Nayeem for many helpful discussions. This work was supported by NSF, Solid State Chemistry Grant #DMR 81-02047.

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