Dislocation-Loop Theory of the Nematic–Smectic A–Smectic C Multicritical Point

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The results of a dislocation-loop theory of the nematic–smectic A–smectic C multicritical point are presented. A new, biaxial nematic phase is found to intervene between the nematic and smectic-C phases. These four phases meet at a decoupled tetracritical point.

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Since the discovery[1] in 1977 of mixtures that display nematic (N), smectic-A (A), and smectic-C (C) phases, the NAC point where these phases meet (see Fig. 1) has been of considerable experimental[1,2] and theoretical[3] interest. Detailed theoretical understanding has thus far been confined to mean-field theory, scaling arguments, and an expansion[4] about 5, the upper critical dimension of Chen and Lubensky's[3] Lifshitz-point model of the NAC point. In this paper we present a dislocation-loop theory of this multicritical point in three dimensions. This theory makes a surprising prediction: Four, rather than three, phases meet at the point where the smectic A–nematic (AN) and smectic A–smectic C (AC) phase boundaries cross (Fig. 2). The new phase, a biaxial nematic[5] (N'), intervenes between the C and N phases and is intermediate between them in its properties. It exhibits the orientational long-range order of the C phase; that is, the smectic layers are tilted in a fixed direction[6] (characterized by their unit normals, $\hat{s}$) relative to the nematic director $\hat{n}$. Its translational properties are those of the nematic: The layers have only short-range positional order,[6] in contrast to the C phase which possesses quasi long-range positional layered order.[6] Thus, sufficiently close to the NAC point, the NC transition, which is first order far from this point and is characterized by the simultaneous onset of long-range orientational and quasi long-range positional order, occurs in two stages, through the N' phase. The system acquires orientational long-range order at the NN' transition and quasi long-range positional order at the CN' transition. Both of these transitions are continuous. N' is therefore a three-dimensional (3D) analog of the (2D) hexatic[7] phase which sometimes separates the 2D solid and liquid states, allowing a two-stage, continuous melting process. The multicritical properties of the $NACN'$ point are exceedingly simple: Our theory predicts that the degrees of freedom describing the NA and AC transitions completely decouple. This implies that these two phase boundaries cross at a finite angle, and pass through each other unaffected. The AC and NN' boundaries thus form a single continuous curve, through the $NACN'$ point, as do the AN and CN' lines. The critical properties of the $NACN'$ point are therefore just a simple superposition of those of the AN (or CN') and AC (or NN') transitions and fall respectively into the universality classes of the XY[8] and inverted XY transitions.[9,10] In the language of magnetic systems, the $NACN'$ point is a decoupled tetracritical point.[11]

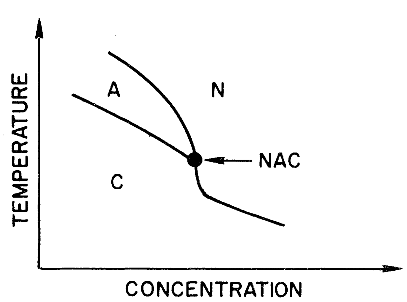

FIG. 1. Experimental phase diagram of the NAC system. The NC transition is first order.

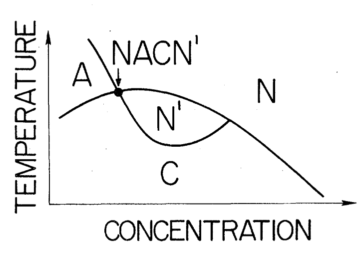

FIG. 2. Phase diagram predicted by the dislocation-loop theory. Its crucial feature is the $NACN'$ point, which replaces the NAC point of Fig. 1. As discussed in the text, N' may be unobservably small. Though the NN' and $N'C$ transitions are both continuous sufficiently close to the $NACN'$ point, one or both of them must contain a tricritical point. The $NN'C$ is then either a critical end point or a triple point. The NC transition is first order.

We now briefly outline our calculation which is similar to Toner's[10] dislocation-loop analysis of the NA transition. In this approach the NA line is characterized by the critical growth ("unbinding") of dislocation loops, which are bounded in size at any point in the A phase. The AC line, on the other hand, is characterized by critical fluctuations in the C director or (two-component) "tilt" order parameter[8] $\vec{c}$, which is essentially the angle between the local director and the normal to the local smectic layers. The point of view elaborated here is that the $NACN'$ point represents the simultaneous criticality of these two quantities.

Our starting point is the elastic Hamiltonian appropriate to the A phase near the A-C phase boundary. This Hamiltonian takes the form[12] $H = H_u + H_c + H_{uc}$; here H_u involves only $u(\vec{x})$, the local displacement of the smectic layers; H_c, involving only the two-component tilt order parameter, $\vec{c}$, is the Ginzburg-Landau Hamiltonian for the 3D XY model; and H_{uc} represents the coupling between them. In the C phase, where $\langle\vec{c}\rangle \neq 0$, the value of $\langle\vec{c}\rangle$ gives the orientation (i.e., $\hat{s}$) of the layers relative to the directors ($\hat{n}$).

Description of the NA line and the $NACN'$ point requires careful treatment of the periodicity of H in the layer displacements, i.e., the fact that states of the system described by $[u(\vec{x})]$ and $[u(\vec{x}) + n(\vec{x})a]$, where $n(\vec{x})$ is an arbitrary integer-valued function of $\vec{x}$ and a is the layer spacing, are identical. The effect of this periodicity is to allow for the existence of quantized topological defects—dislocation loops in this case. As discussed in Refs. 9, 10, and 13, these loops can be characterized by an integer-valued vector field $\vec{m}$ which points along the dislocation loop and whose magnitude counts the number of extra layers inserted to create the dislocation. The field u associated with these defects is no longer single valued; it satisfies

$$\nabla \times \nabla u(\vec{x}) = \vec{m}(\vec{x}). \qquad (1)$$

That the dislocations form closed loops is manifest in the constraint that the $\vec{m}$ field be divergenceless: $\nabla \cdot \vec{m} = 0$.

Following Kosterlitz and Thouless[14] and Nelson and Toner,[13] we decompose u and $\vec{c}$ into "spin-wave" and dislocation parts: $u = u_S + u_D$ and $\vec{c} = \vec{c}_S + \vec{c}_D$. This decomposition is uniquely defined by the requirements that u_S be smooth and single valued while u_D and $\vec{c}_D$ minimize the Hamiltonian (H), i.e.,

$$\delta H/\delta u|_{u=u_D,\, \vec{c}=\vec{c}_D} = \delta H/\delta\vec{c}|_{u=u_D,\, \vec{c}=\vec{c}_D} = 0, \qquad (2)$$

subject to the constraint (1). Solving these Euler-Lagrange equations and (1) simultaneously, we express u_D and $\vec{c}_D$ in terms of $\vec{m}$. In practice this is done perturbatively in the anharmonic terms of H. Inserting the resulting expressions for u_D and $\vec{c}_D$ back into (1), we obtain a Hamiltonian involving only the single-valued fields u_S, c_S, and $\vec{m}$. A series of duality and other transformations essentially identical to those of Ref. 10 are then used to handle the divergencelessness and integer valuedness of the $\vec{m}$'s, thereby mapping the model onto a gauge theory involving a complex scalar field ψ, a two-component vector potential $\vec{A}$, and the fields u_S and $\vec{c}_S$. The field ψ acts as a *disorder* parameter for translational order in that it is nonzero in the translationally disordered phases (N' and N) and vanishes in the translationally quasiordered A and C phases.[10] The Hamiltonian for this gauge model, analytically continued to d dimensions where both $\vec{A}$ and $\vec{c}_S$ have $d-1$ components, takes the form

$$H = \tfrac{1}{2}\int d^d r \{\tilde{r}|\psi|^2 + 2u_\psi|\psi|^4 + |(\nabla - i\vec{A})\psi|^2 + r|\vec{c}_S|^2 + 2v|\vec{c}_S|^4 + K_1{}^c|\nabla_\perp\cdot\vec{c}_S|^2 + K_2{}^c|\nabla_\perp\times\vec{c}_S|^2 + K_3{}^c|\partial_z\vec{c}_S|^2 + 4w|\vec{c}_S|^2|\psi|^2\} + \tfrac{1}{2}\textstyle\sum_{\vec{q}}(q_\perp{}^2/B + q_z{}^2/K' q_\perp{}^2)|\vec{A}_{\vec{q}}|^2, \qquad (3)$$

where $K' = K_1 - g_2{}^2/4K_1{}^c$, K_1, B, r, v, g_2, $K_1{}^c$, $K_2{}^c$, and $K_3{}^c$ were defined in Ref. 12, and $\tilde{r}$, u_ψ, and w are coupling constants introduced in the implementation of the various transformations. (Similar Hamiltonians were postulated on a phenomenological basis by Chu and McMillan, by Benguigi, and Huang and Lien. See Ref. 3.) The parameter $\tilde{r}$ controls the system's proximity to the AN phase boundary, though, because of the duality transformations, the temperature axis has been reversed; that is, as $\tilde{r}$ increases, the system moves towards (or deeper into) the A phase.[10] In the absence of coupling between the $\vec{c}_S$ and ψ fields [i.e., with $w=0$ in (3)], H decomposes into the sum of two independent Hamiltonians, one a gauge theory involving the ψ and $\vec{A}$ fields, the other involving only $\vec{c}_S$. The latter of these obviously describes an XY model. In Ref. 10 the former was likewise shown to fall, insofar as thermodynamic properties are concerned, in the universality class of the XY model, though with an inverted temperature axis. With $w=0$, therefore, the multicritical point, characterized by the simultaneous vanishing of the appropriately renormalized versions of r and $\tilde{r}$, is described by a "decoupled" fixed point composed of two independent XY fixed points. The mutual independence of the transitions implies that the two phase boundaries pass smoothly through each other at the $NACN'$ point, producing a phase diagram with the (tetracritical) topology of Fig. 2. In the N' phase both $\vec{c}_S$ and ψ have nonvanishing expectation values which respectively imply the presence of orientational long-range order and the absence of positional long-range order.

The effect of the term coupling ψ and $\vec{c}_S$ in (3) has been studied by Aharony[11] in the context of models of the bicritical point. He has shown that the renormalization-group eigenvalue whose sign determines the relevance of the coupling operator is exactly given by $2\lambda = \alpha_1/\nu_1 + \alpha_2/\nu_2$; the α's and ν's are respectively the specific heat and correlation-length exponents for the two (ψ and $\vec{c}_S$) decoupled transitions. Since α is slightly negative,[15] ($\alpha \approx -0.2$) for the 3D XY model, the coupling is *irrelevant* at the transition. The conclusions stated at the start of this paper follow immediately; in particular, a biaxial nematic phase must intervene between the C and N phases, at least sufficiently close to the decoupled multicritical point.

The decoupling also implies that the AC and NN' transitions are identical; both are just ordering transitions for the $\vec{c}_S$ field and so fall in the universality class of the isotropic XY model.[16] Likewise the AN and CN' transitions are identical loop-unbinding transitions, and hence inverted-XY-like.[10]

None of the experimental studies[1,2] of the NAC point has reported the existence of a new, fourth phase at that point. There is at least one plausible explanation for this. If the coefficients w, u_ψ, and v in (2) satisfy $w^2 > u_\psi v$ then mean-field theory predicts[11] a bicritical phase diagram with no N' phase and a direct first-order N-C transition. Though the renormalization-group analysis implies the existence of the N' phase at the multicritical point, the mean-field result must hold sufficiently far from this point. The size of the N' phase depends on the ratio $R = w^2/u_\psi v$. When $R \gg 1$ one has to get very close to the multicritical point before the mean-field prediction of a single first-order NC transition breaks down; the N' phase will in consequence be tiny. This explanation also suggests which systems might be most likely to violate $R > 1$ and hence display an observable intermediate N' phase: those with a short bare correlation length for $\vec{c}$ fluctuations (e.g., p-nonyloxybenzoate-p-butyloxyphenol, also known as $\bar{9}O\bar{4}$), for which the AC transition might not be mean field,[17] implying a fairly large v. Experimental studies of such systems would be of interest in light of the results of this paper.

Given that the parameters of the problem are such as to produce the topology of Fig. 2, it remains to elucidate the order of the NN' and $N'C$ transitions. Our argument that both are continuous applies only sufficiently close to the multicritical point. It is necessary that one or both of them become first order at a tricritical point before they intersect at the $NN'C$ juncture. (Were they both to remain second order until they merge to form the first-order NC boundary at the $NN'C$ point then the $NN'C$ point would be bicritical. We have already demonstrated that such a bicritical point is unstable.) If both $N'C$ and NN' become first order, then $NN'C$ is a triple point; if only one does, $NN'C$ is a critical end point.

The dislocation-loop approach employed here can readily be modified to produce theories of the NAC point in a strong magnetic field and of the $m=n=2$ Lifshitz point.[4] Details will be relegated to a separate publication.

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[1] D. Johnson, D. Allender, R. De Hoff, C. Maze, E. Oppenheim, and R. Reynolds, Phys. Rev. B 16, 470 (1977); G. Sigaud, F. Hardouin, and M. Achard, Solid State Commun. 23, 35 (1977).

[2] R. De Hoff, R. Biggers, D. Brisbin, and D. L. Johnson, Phys. Rev. A 25, 472 (1982); R. De Hoff, R. Biggers, D. Brisbin, R. Mahmood, C. Gooden, and D. L. Johnson, Phys. Rev. Lett. 47, 664 (1981); C. R. Safinya, R. J. Birgeneau, J. D. Litster, and M. E. Neubert, Phys. Rev. Lett. 47, 668 (1981).

[3] J.-h. Chen and T. Lubensky, Phys. Rev. A 14, 1202 (1976); K. Chu and W. McMillan, Phys. Rev. A 15, 1181 (1977); L. Benguigui, J. Phys. (Paris), Colloq. 40, C3-222 (1979); C. C. Huang and S. C. Lien, Phys.

Rev. Lett. 47, 1917 (1981).

[4]R. M. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. 35, 1678 (1975); G. S. Grest and J. Sak, Phys. Rev. B 17, 3607 (1978). The Chen-Lubensky model differs from the Lifshitz-point model studied in these references by the inclusion of director fluctuations; these, however, can be shown to be irrelevant near $d = 5$. (G. Grinstein and R. Pelcovits, unpublished.)

[5]This name is not intended to imply that this phase has inversion symmetry in all three directions [it only has this symmetry in one direction, like the C phase; see, e.g., P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, Oxford, 1974)]. Rather, it refers to the fact that the phase is characterized by broken orientational order in two directions, instead of one as in a conventional nematic.

[6]de Gennes, Ref. 5.

[7]See, e.g., B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. 41, 121, 519(E) (1978); D. R. Nelson and B. I. Halperin, Phys. Rev. B 19, 1347 (1979); T. F. Rosenbaum, S. E. Nagler, P. M. Horn, and R. Clarke, Phys. Rev. Lett. 50, 1791 (1983).

[8]See, e.g., P. G. de Gennes, C. R. Acad. Sci. 274, 758 (1972), and Mol. Cryst. Liq. Cryst. 21, 49 (1973); G. Grinstein and R. A. Pelcovits, Phys. Rev. A 26, 2196 (1982), and references therein.

[9]C. Dasgupta and B. I. Halperin, Phys. Rev. Lett. 47, 1556 (1981). Thermodynamic properties of an inverted XY transition are identical to those of the regular XY model with an inverted temperature axis.

[10]J. Toner, Phys. Rev. B 26, 402 (1982).

[11]M. E. Fisher and D. R. Nelson, Phys. Rev. Lett. 32, 1350 (1974); D. R. Nelson, J. M. Kosterlitz, and M. E. Fisher, Phys. Rev. Lett. 33, 813 (1974), and Phys. Rev. B 13, 412 (1976); A. Aharony, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, and Bull. Am. Phys. Soc. 20, 16 (1975).

[12]Grinstein and Pelcovits, Ref. 8, and references therein.

[13]W. Helfrich, J. Phys. (Paris) 39, 1199 (1978); M. Peskin, Ann. Phys. (N.Y.) 113, 122 (1978); R. Savit, Rev. Mod. Phys. 52, 453 (1980); C. Dasgupta, Phys. Rev. A 27, 1261 (1983); D. R. Nelson and J. Toner, Phys. Rev. B 24, 363 (1981).

[14]J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973); J. M. Kosterlitz, J. Phys. C 7, 1046 (1974).

[15]See, e.g., D. D. Betts, in *Phase Transitions and Critical Phenomena* (Academic, London, 1976), Vol. 3.

[16]It is important to note that though the asymptotic AC transition is XY like, the asymptotic region is typically unobservably small and experimentally the transition appears mean-field-like. See, e.g., C. C. Huang and J. M. Viner, Phys. Rev. A 25, 3385 (1982); Huang and Lien, Ref. 3; M. Miechle and C. W. Garland, Phys. Rev. A 27, 2624 (1983), and references therein.

[17]M. Delaye, J. Phys. (Paris), Colloq. 40, C3-350 (1979).