Multicriticality in Hexatic Liquid Crystals

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A theory is presented for the successive sixfold Fourier components, C_{6n}, in the bond-orientational order in the neighborhood of a smectic-*A*–hexatic-*B* phase transition. Near the transition we predict that $C_{6n} \sim C_6^{\sigma_n}$ with $\sigma_n = n + x_n n(n-1)$ where x_n depends weakly on *n*. General arguments are presented for the topology of the phase diagram in the vicinity of the smectic "liquid-hexatic-crystal" triple point which lead to the existence of a tricritical point on the smectic-*A*–hexatic-*B* line.

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In recent years it has been realized that there are bulk phases of matter with bond-orientational long-range order as in a solid but positional short-range order as in a fluid. Examples include the hexatic-*B* phase of liquid crystals and icosahedral metallic glasses.[1] In the liquid-crystal hexatic phases there is long-range sixfold-symmetric orientational alignment of the lines connecting neighboring molecules in the smectic planes. This order is characterized by a local order parameter $\psi(\mathbf{r}) = e^{6i\theta(\mathbf{r})}$, where θ is the angle between the "bonds" and some reference axis.[2] In-plane positional order, characterized by the density Fourier components $\rho_{\mathbf{q}}$, is achieved at a lower temperature. Recent research has concentrated on two main phase sequences. In some materials, such as *n*-hexyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) and mixtures containing it, one observes[3] the sequence smectic $A \rightarrow$ hexatic $B \rightarrow$ crystal E ($S_A \rightarrow S_{BH} \rightarrow S_E$). The temperature range of the hexatic phase is usually narrow. In other liquid crystals, such as 4O.8, a direct transition from S_A to a crystal, S_{BC}, is observed.[4] Mixtures of the two types of materials exhibit a triple point, at which the S_A, S_{BH}, and S_{BC} phases coexist.[5] In many of these systems, the transition from S_A to S_{BH} is continuous, but has a tricritical specific-heat exponent, $\alpha \simeq 0.5$.[6] In others, the transition appears to be weakly first order. For cases in which the crystal phase also has long-range herringbone order such as S_E, the existence of such a tricritical point has been attributed to the coupling of the bond-orientational order with herringbone order.[7] An alternative phase sequence involves smectic $C \rightarrow$ tilted hexatic $I \rightarrow$ crystal J ($S_C \rightarrow S_I \rightarrow S_J$), as in racemic 4-(2-methylbutyl)phenyl 4′-(octyloxy)-(1,1′)-biphenyl-4-carboxylate (8OSI).[8] In this case the coupling to molecular tilt induces long-range hexatic order even in the S_C phase.[2,8] This coupling allows the growth of single-domain samples, which in turn has recently made possible a direct measurement of many of the 6*n*-fold order parameters[8] $C_{6n} = \mathrm{Re}\langle \psi^n \rangle = \mathrm{Re}\langle e^{6in\theta} \rangle$.

In the present Letter we discuss in detail the theoretical origins of the power laws $C_{6n} \sim C_6^{\sigma_n}$ observed in the synchrotron x-ray studies of the $S_C \rightarrow S_I$ transition in 8OSI. We note that the exponents σ_n are related to a sequence of crossover exponents,[9] associated with symmetry-breaking terms which describe multicritical crossover from the *XY*-model critical behavior into that of uniaxial ($n=20$),[10] three-state Potts model ($n=3$),[11] cubic ($n=4$), hexagonal ($n=6$),[12] etc., symmetry. Although the crossover exponents for $n=2$ and $n=3$ were measured separately before,[10,11] the present method allows a simultaneous measurement of many of these exponents, including those with $n \geqslant 4$ which usually only represent corrections to scaling, and which are accordingly very difficult to measure. The sequence σ_n represents an infinite set of independent critical exponents, all of which characterize the critical behavior. As we discuss below, a detailed analysis of the *n* dependence of σ_n is quite illuminating. Since averages like $\langle \psi^n \rangle$ always appear as Fourier coefficients in phase transitions characterized by a complex order parameter,[9] similar phenomena should occur near a variety of incommensurate phase transitions,[9] and in other systems such as certain graphite intercalates.[13]

As we show below, the data on 8OSI are fully consistent with the theoretical predictions on C_{6n}. In addition, we find some indications that the transition may be nearly tricritical, similar to those in many $S_A \rightarrow S_{BH}$ systems.[6] Since the coupling to the herringbone order is unimportant in 8OSI, we present an alternative thermodynamic argument, which suggests that the $S_A \rightarrow S_{BH} \rightarrow S_{BC}$ phase diagram should always have the structure shown in Fig. 1, with a tricritical

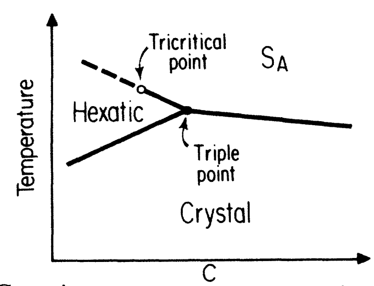

FIG. 1. Generic temperature-concentration phase diagram near the S_A-S_{BH}-S_{BC} coexistence triple point. The broken (full) lines indicate second- (first-) order transitions.

point and a triple point. The same structure should apply to the $S_C \to S_I \to S_J$ sequence although the second-order $S_C \to S_I$ transition will be rounded by the small hexatic field created by the molecular tilt. We hope that the present paper will stimulate much more detailed experiments in the vicinity of the triple point as well as detailed measurements of the successive Fourier components in other systems mentioned above.

Our theoretical analysis of the S_A-S_{BH} and S_C-S_I transitions starts from the Ginzburg-Landau Hamiltonian,[2]

$$\bar{H} = \int d^d r \{ \tfrac{1}{2} |\nabla\psi|^2 + \tfrac{1}{2} r |\psi|^2 + u_4 |\psi|^4 + u_6 |\psi|^6 + h \operatorname{Re}\psi \}. \quad (1)$$

Here the ordering field h is determined[2] by the average tilt order parameter, ϕ $(h \sim \phi^6)$; it is zero for S_A phases while the experimental results indicate that h is quite small in S_C phases. For $h=0$, this model exhibits XY-model critical behavior, provided that u_4 is larger than a tricritical value, u_{4t}. At $u_4 = u_{4t}$, Eq. (1) has a tricritical point, characterized for $d \geqslant 3$ dimensions by the Gaussian fixed point, with mean-field exponents and logarithmic corrections.

To study $C_{6n} = \operatorname{Re}\langle\psi^n\rangle$, we add to Eq. (1) a field term $\bar{H}_n = g_n \int d^d r \operatorname{Re}(\psi^n)$. The essential observation is that if one writes $\psi = x + iy$, one sees that successive terms $n = 2, 3, 4$, etc., scale like the uniaxial $(x^2 - y^2)$, Potts $(x^3 - 3xy^2)$, cubic $4(x^4 + y^4) - 3|\psi|^4$, etc., anisotropies.[9–11] Asymptotically close to the XY-model fixed point, the free energy should scale as $F(t, g_n) = |t|^{2-\alpha} f(g_n / |t|^{\phi_n})$, where $t = (T - T_c)/T_c$, α is the XY specific-heat exponent, and ϕ_n the appropriate crossover exponent.[9,10] Thus,

$$C_{6n} = (\partial F / \partial g_n)_{g_n = 0} \sim |t|^{2-\alpha-\phi_n} \sim C_y^{\sigma_n}, \quad (2)$$

with

$$\sigma_n = \frac{2 - \alpha - \phi_n}{2 - \alpha - \phi_1} = \frac{2(d - \lambda_n)}{d - 2 + \eta}, \quad (3)$$

where $\lambda_n = \phi_n / \nu$. This behavior holds only asymptotically close to the XY transition. As we show below, in that limit $\sigma_n = n + x_n n(n-1)$ with x_n weakly dependent on n.

Generally, one is not asymptotically close to the XY transition so that C_6 may not be small and there is typically a nearby tricritical point. In mean-field theory $\sigma_n = n$, so that at a tricritical point one should have simply $C_{6n} \sim C_6^n$ plus logarithmic corrections. Therefore, it is necessary to consider carefully the crossover from Gaussian to XY behavior. To leading order in $\tilde{u}_4 = (u_4 - u_{4t})$, the renormalization-group recursion relation for g_n is $dg_n/dl = y_n^0 g_n - 4K_d \tilde{u}_4 n(n-1) g_n$, where $y_n^0 = d - n(d - 2 + \eta)/2$. The factor $n(n-1)$ comes from the combinatorics of picking two out of the n factors in ψ^n, and appears in all higher-order terms as well.[10,14] Using the solutions[15] $\tilde{u}_4(l) = \tilde{u}_4 e^{\epsilon l} / Q(l)$, $t(l) = t e^{2l} / Q(l)^{2/5}$, we find that

$$g_n(l) = g_n \exp(y_0^n l) / Q(l)^{n(n-1)/10},$$

with $Q(l) = 1 + (\tilde{u}_4 / u_4^*)(e^{\epsilon l} - 1)$, $4K_d u_4^* = \epsilon/10$, and $\epsilon = 4 - d$. Substituting in $F(t, g_n) = e^{-dl} F(t(l), g_n(l))$, we find that

$$C_{6n}(t, h) = \exp[-(d - y_n^0) l] Q(l)^{-n(n-1)/10} C_{6n}(t(l), \exp(y_1^0 l) h).$$

We now iterate our recursion relations until $C_6(t(l^*), \exp(y_1^0 l^*) h) = 1$. Since at that point C_{6n} will also be of order unity, we conclude that

$$C_{6n} \simeq C_6^n [1 + (\tilde{u}_4 / u_4^*)(C_6^{-2\epsilon/(d-2+\eta)} - 1)]^{-n(n-1)/10}. \quad (4)$$

Note that the dependence on t and h has dropped out.

Equation (4) is correct for all dimensionalities $d \geqslant 3$ near the tricritical point where $\tilde{u}_4$ is small. It should also work well whenever C_6 is not too small, so that l^* is not too large. When the ratio $\rho = C_6^2 / (\tilde{u}_4 / u_4^*)$ is much less than 1, one is in the asymptotic XY regime and (4) reduces to (2) with $C_{6n} = C_6^{\sigma_n}$, with $\sigma_n = n + x_n n(n-1)/(d-2+\eta)$ and $x_n = \epsilon/5 + O(\epsilon^2)$. When ρ is not small, the C_6^{-2} term must remain inside the brackets of (4), and can represent an important correction because of the $n(n-1)$ exponent. In the 8OSI experiments, the C_{6n} are most easily measured when C_6 is large, so that ρ may not be small. Even under these circumstances, both (2) and (4) predict that the correction to the mean-field result $C_{6n} \sim C_6^n$ scales like a temperature-dependent constant raised to the power $n(n-1)$. In fact, if we take $x_n = \lambda(T)$ to be independent of n, the two forms are identical with $(\tilde{u}_4 / u_4^*) = (C_6^{-10\lambda(T)} - 1)/(C_6^{-2} - 1)$ in $d = 3$.

We next consider the asymptotic XY regime $\rho \ll 1$. Using the ϵ-expansion results[14] to order ϵ^3, one has

$$x_n \simeq \tfrac{1}{5}\epsilon\{1 + \tfrac{1}{5}\epsilon(3 - n) + \tfrac{1}{25}\epsilon^2(n^2 + 3.366\,455 n - 22.322\,657)\}.$$

Clearly, extrapolation to $\epsilon = 1$ is not trivial. Simple substitution of $\epsilon = 1$ in this equation shows that x_n increases from ~ 0.15 to ~ 0.4 for $n = 2$ to 7. An alternative estimate of x_n may be obtained by use of the values of u_4^* and the diagrammatic integrals in $d = 3$ directly rather than in $d = 4 - \epsilon$. Taking the numbers of Jug[16] to order $(u_4^*)^2$

we find $x_n \simeq 0.3-0.008n$ or $x_n \simeq 0.3/(1+0.027n)$. This form yields a much weaker dependence on n, with x_n varying from 0.3 to 0.25 for $n=2$ to 7. To summarize, at $d=3$ Eq. (4) holds for $C_6 > (\tilde{u}_4/u_4^*)^{1/2}$; for smaller C_6 it simplifies to $C_{6n} \sim C_6^{\sigma_n}$ with $\sigma_n = n + x_n n(n-1)/(d-2+\eta)$.

Given the above theoretical predictions, we have reanalyzed the data on 8OSI.[8] We first fitted the measured angular structure factor at each temperature by the form

$$S(\chi) = I_0\left\{\frac{1}{2} + \sum_{n=1}^{\infty} C_{6n}\cos[6n(90-\chi)]\right\} + I_{BG}, \quad (5)$$

with $C_{6n} = C_6^{\sigma_n}$. The resulting average effective exponents σ_n, already reported in Ref. 8, are shown in Fig. 2. As emphasized in Ref. 8, Eq. (5) is chosen such that as $\psi \to 1$ each $C_{6n} \to 1$ so that the C_{6n} are properly normalized. Thus it is plausible that the proportionality sign in Eq. (2) would become an equality and this has been assumed in the analysis. As seen in the figure, the results fit well with $\sigma_n = n + 0.295n(n-1)$ consistent with the theory. From Eq. (3), with the XY values $\nu \simeq 0.67$, $\eta \sim 0.03$, our results give $\phi_2 = 1.16 \pm 0.07$ and $\phi_3 = 0.4 \pm 0.17$, consistent with earlier measurements.[10,11] Our results also yield $\beta_6 = (d-\lambda_6)\nu = 5.1 \pm 0.4$, which is higher than the ϵ-expansion estimate 3.59 in Ref. 2.

We next fitted Eq. (5) to the data of Ref. 8 assuming $C_{6n} = C_6(T)^{n+\lambda(T)n(n-1)}$, and the resulting $C_6(T)$ and $\lambda(T)$ are shown in Fig. 3. For $T < 77.6\,^\circ\mathrm{C}$, that is $C_6 > 0.47$, $\lambda(T)$ is practically a constant, $\lambda(T) \simeq 0.295 \pm 0.02$. This may be compared with the theoretical XY value $x_n = 0.3 - 0.008n$. Fixing $\lambda(T)$ at 0.295 for all T indeed gives comparable fits, with the goodness-of-fit parameter χ^2 typically between 1 and 2. Identical fits are obtained with Eq. (4) with $\tilde{u}_4/u_4^* = 1.7$ so that $\rho \sim 0.4$. In the transition region $\lambda(T)$ appears to decrease towards zero suggesting a crossover to mean-field (tricritical?) behavior; however, much more precise data are required to establish this definitively.

Finally, in Ref. 8 fits were performed with no restrictions whatsoever on the C_{6n}. If we write $C_{6n} = a_n C_6^{\sigma_n}$ and fit all of the data for $T < 76.8\,^\circ\mathrm{C}$ for each C_{6n} we find excellent fits with a_n varying from 0.99 to 0.73 as n varies from 2 to 6 and the exponents follow the law $\sigma_n = n + 0.22n(n-1)$. These results are consistent with the constrained fits at individual temperatures discussed above.

As noted above, the essential feature of both Eqs. (2) and (4) is that the correction to the mean-field result $C_{6n} \sim C_6^n$ scales like some temperature-dependent constant raised to the power $n(n-1)$. Since Eq. (4) applied away from the critical point, choosing the amplitude factor to be 1 is correct to leading order; however, writing $C_{6n} = C_6^{\sigma_n}$ in the critical regime is a much stronger assumption. The 8OSI data, nevertheless, seem to support this assumption; presumably the fact that Eqs. (2) and (4) must connect continuously means that the proportionality factor in Eq. (2) cannot deviate significantly from 1. The actual value for $\lambda(T)$ agrees remarkably well with the theoretical estimate, $x_n = 0.3 - 0.008n$ for the asymptotic XY regime in spite of the fact that C_6 is as large as 0.9. Much better data than those currently available, especially in the regime where C_6 is small, will be required to differentiate between Eqs. (2) and (4) and to determine whether or not the crossover to mean-field behavior [$\lambda(T) \to 0$] near T_c suggested by Fig. 3 is real.

The beauty of the above analysis is that the finite ordering field h in the tilted hexatic has not hidden in-

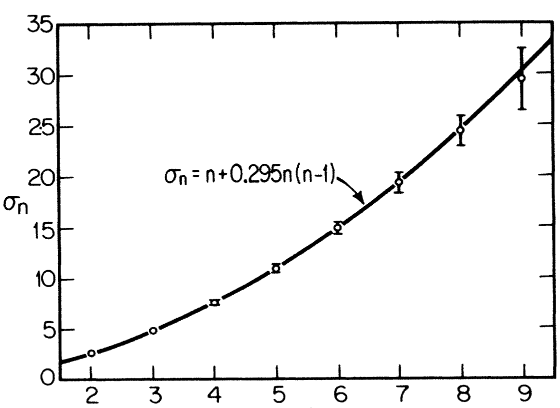

FIG. 2. Measured exponents σ_n from Ref. 8. The line is $\sigma_n = n + 0.295n(n-1)$.

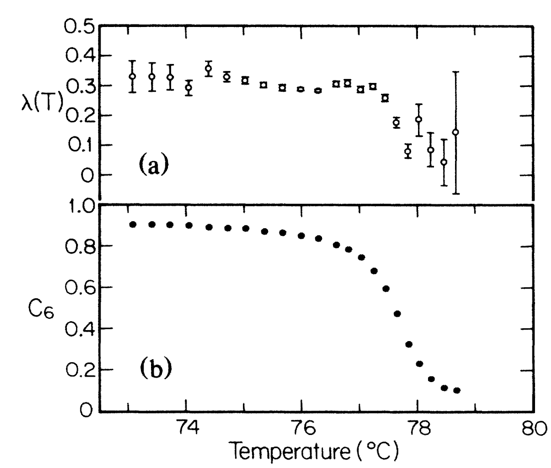

FIG. 3. (a) $\lambda(T)$ and (b) $C_6(T)$, from fits of the 8OSI data of Ref. 8 to Eq. (5), with $C_{6n} = C_6(T)^{\sigma_n}$, $\sigma_n = n + \lambda(T)n(n-1)$.

teresting behavior but rather has made possible a direct measurement of C_{6n}. The situation is more difficult if we wish to identify other critical exponents, such as β or δ. We fitted C_6 to a parametric equation of state,[17] $h=\theta(1-\theta^2)r^{\beta+\gamma}$, $C_6=K\theta r^{\beta}$, $t=(1-b^2\theta^2)r$, in which β, γ, T_c, K, and h were parameters. Data from 73 to 81 °C could be fitted, but gave a small value of β suggesting the possibility of a weakly first-order transition. When only $C_6<0.8$ were fitted, we obtained $\gamma\simeq 1$ and $\beta\simeq 0.25$. Fits of the same range of data to Eq. (1) without the gradient term gave small negative values of u_4. These results are also suggestive of a tricritical point, as found in Refs. 3–6. The sharp changes in the order parameter C_6 near 77 °C are remininscent of the behavior near a wing tricritical line close to a tricritical point.[18]

We now present arguments explaining why such a tricritical point must occur, due to the nearby coexistence point of S_A, S_{BH}, and S_{BC} or, ignoring the rounding effect of the induced h, S_C, S_I, and S_J. The transition $S_A \rightarrow S_{BC}$ or $S_C \rightarrow S_J$ is always first order, due to the cubic term in the crystalline order parameter,[19] $\rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3}$ with $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0$. The same cubic term survives in the S_{BH} (S_I) phase, and turns the $S_{BH}\rightarrow S_{BC}$ ($S_I\rightarrow S_J$) transition first order as indeed observed in 8OSI. These two first-order lines meet at the triple point with different slopes (see Fig. 1), since the coupling between ψ and ρ (or order $|\psi|\rho^2$) shifts the transition $S_{BH}\rightarrow S_{BC}$ ($S_I\rightarrow S_J$) relative to the continuation of the $S_A\rightarrow S_{BC}$ ($S_C\rightarrow S_J$) line. This discontinuity in slope at the triple point now implies a discontinuity across the $S_A\rightarrow S_{BH}$ ($S_C\rightarrow S_I$) line in that vicinity, turning it first order.[20] As one moves away from the triple point the effects of ρ on fluctuations in ψ decrease, and the effective coefficient $\tilde{u}_4$, obtained after elimination of ρ from the partition function, may change sign.[21]

Since the $S_I\rightarrow S_J$ transition in 8OSI occurs only about 4 °C in temperature below the rounded $S_C\rightarrow S_I$ transition, we expect a triple point to exist nearby in some extended parameter space such as concentration or pressure. Further experiments are needed to confirm Fig. 1 for 8OSI and for the many cases discussed in Refs. 3–6.

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[1]R. J. Birgeneau and J. D. Litster, J. Phys. (Paris), Lett. **39**, 1399 (1978); B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); P. W. Stephens and A. Goldman, Phys. Rev. Lett. **56**, 1168 (1986).

[2]D. R. Nelson and B. I. Halperin, Phys. Rev. B **21**, 5312 (1980); R. Bruinsma and D. R. Nelson, Phys. Rev. B **23**, 402 (1981).

[3]R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981); C. Rosenblatt and J. T. Ho, Phys. Rev. A **26**, 2293 (1982); R. Mahmood, M. Lewis, R. Biggers, V. Surendranath, D. L. Johnson, and M. E. Neubert, Phys. Rev. A **33**, 519 (1986); J. M. Viner, D. Lamey, C. C. Huang, R. Pindak, and J. W. Goodby, Phys. Rev. A **28**, 2433 (1983).

[4]P. S. Pershan, G. Aeppli, J. D. Litster, and R. J. Birgeneau, Mol. Cryst. Liq. Cryst. **67**, 205 (1981); D. E. Moncton and R. Pindak, Phys. Rev. Lett. **43**, 701 (1979).

[5]J. W. Goodby, Mol. Cryst. Liq. Cryst., Lett. Sect. **72**, 95 (1981); J. W. Goodby and R. Pindak, Mol. Cryst. Liq. Cryst. **75**, 233 (1981).

[6]T. Pitchford, G. Nounesis, S. Dumrongrattana, J. M. Viner, C. C. Huang, and J. W. Goodby, Phys. Rev. A **32**, 1938 (1985); C. C. Huang, private communication.

[7]R. Bruinsma and G. Aeppli, Phys. Rev. Lett. **48**, 1625 (1982).

[8]J. D. Brock, A. Aharony, R. J. Birgeneau, K. W. Evans-Lutterodt, J. D. Litster, P. M. Horn, G. B. Stephenson, and A. R. Tajbakhsh, Phys. Rev. Lett. **57**, 98 (1986).

[9]R. A. Cowley and A. D. Bruce, J. Phys. C **11**, 3577 (1978).

[10]M. E. Fisher and P. Pfeuty, Phys. Rev. B **6**, 1889 (1972); F. J. Wegner, Phys. Rev. B **6**, 1891 (1972); for reviews see (theory) A. Aharony, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), p. 357; (experiment) Y. Shapira, in *Multicritical Phenomena,* edited by R. Pynn and A. Skjeltrup (Plenum, New York, 1984), p. 35.

[11]A. Aharony, K. A. Müller, and W. Berlinger, Phys. Rev. Lett. **38**, 33 (1977), and references therein.

[12]D. R. Nelson, Phys. Rev. B **13**, 2222 (1976).

[13]See, for example, P. Bak, Phys. Rev. Lett. **44**, 889 (1980).

[14]F. J. Wegner and A. Hougton, Phys. Rev. A **10**, 435 (1974); D. J. Wallace, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), p. 293.

[15]D. R. Nelson and J. Rudnick, Phys. Rev. B **13**, 2208 (1976).

[16]G. Jug, Phys. Rev. B **27**, 609 (1983).

[17]J. T. Ho and J. D. Litster, Phys. Rev. B **2**, 4523 (1970).

[18]See, e.g., D. Mukamel and M. Blume, Phys. Rev. A **10**, 610 (1974).

[19]S. Alexander and J. P. McTague, Phys. Rev. Lett. **40**, 702 (1978).

[20]J. Wheeler, J. Chem. Phys. **61**, 4474 (1974).

[21]A similar phenomenon was discussed by E. Domany, D. Mukamel, and M. E. Fisher, Phys. Rev. B **15**, 5432 (1977).