Liquid Crystals in Two Dimensions: First-Order Phase Transitions and Nonuniversal Critical Behavior

R. L. C. Vink

Institut für Theoretische Physik II, Heinrich Heine Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany

(Received 20 October 2006; revised manuscript received 27 February 2007; published 21 May 2007)

Liquid crystals in two dimensions undergo a first-order isotropic-to-quasi-nematic transition, provided the particle interactions are sufficiently "sharp and narrow." This implies phase coexistence between isotropic and quasi-nematic domains, separated by interfaces. The corresponding line tension is determined and shown to be very small, giving rise to strong interface fluctuations. When the interactions are no longer "sharp and narrow," the transition becomes continuous, with nonuniversal critical behavior obeying hyperscaling and approximately resembling the two-dimensional Potts model.

DOI: 10.1103/PhysRevLett.98.217801 PACS numbers: 64.70.Md, 05.50.+q, 64.60.Cn, 64.60.Fr

Fluids consisting of elongated molecules can form nematic phases. In the nematic phase, the molecules are aligned, which distinguishes it from the isotropic phase, where the molecular orientations are random. The nematic phase is the standard example of a liquid crystal. Consequently, its properties are of fundamental importance. The nematic phase can be prepared in several ways. In thermotropic liquid crystals, the isotropic-to-nematic (I-N) transition is temperature driven: starting in the high-temperature isotropic phase, the nematic phase is reached by lowering the temperature. The Lebwohl-Lasher (LL) model [1] provides a convenient theoretical framework. In this model, a unit vector $\vec{d}_i$ is assigned to each site i of a lattice, where $\vec{d}_i$ represents the orientation of the molecule at the i-th lattice site. The molecules interact with Hamiltonian

$$\mathcal{H} = -\epsilon \sum_{\langle i,j \rangle} |\vec{d}_i \cdot \vec{d}_j|^p, \tag{1}$$

where the sum is over nearest neighbors (factors of $k_B T$ are absorbed in the coupling constant ϵ, with T the temperature, and k_B the Boltzmann constant). In Ref. [1], Eq. (1) is studied in $d = 3$ dimensions with $p = 2$. At low enough temperature, Eq. (1) then undergoes a first-order transition from an isotropic phase to a nematic phase. Nematic phases also occur in lyotropic systems, where density drives the I-N transition. Onsager has shown that infinitely slender rods in $d = 3$ dimensions also undergo a first-order I-N transition, at sufficiently high density [2].

In $d = 3$ dimensions, the I-N transition is well understood. In contrast, the two-dimensional case, which is the topic of this Letter, is more controversial. More precisely, we shall consider Eq. (1) in $d = 2$ spatial dimensions, using two-component unit vectors $\vec{d}_i$. For $p = 2$, Eq. (1) then becomes the XY model [3], and a nematic phase with long-range order is ruled out by the Mermin-Wagner (MW) theorem [4]. The two-dimensional XY model and its variants were thought to be without a phase transition for a long time, until Kosterlitz and Thouless (KT) proved that a phase transition *does* occur, and clarified its topological nature [5]. The KT transition is one from a (high-temperature) isotropic phase, with exponential decay of the angular correlations, to a (low-temperature) quasi-nematic phase, with power-law decay of the correlations. In the XY model, the KT transition is continuous. By lowering the temperature, starting in the isotropic phase, the correlation length grows exponentially, until it diverges at the transition temperature, where the quasi-nematic phase sets in. Since the quasi-nematic phase has infinite correlation length, it is a critical phase. Consequently, the order parameter Δ and the susceptibility χ scale as

$$\Delta \propto L^{-\beta/\nu}, \qquad \chi \propto L^{\gamma/\nu}, \tag{2}$$

with L the system size; β, γ, and ν are the critical exponents of the order parameter, susceptibility, and correlation length, respectively. Since the correlation length diverges exponentially, the exponents themselves are undefined. However, exponent *ratios* are still defined [3,6], via Eq. (2).

Since the XY model and the LL model are similar, the I-N transition in two-dimensional liquid crystals is often assumed to be of the conventional KT type. Clearly, for Eq. (1) with $p = 2$ this is justified. If one then accepts a well-defined universality class for two-dimensional liquid crystals, it seems reasonable that Eq. (1) for arbitrary $p \geq 2$, and indeed also lyotropic liquid crystals, are all qualitatively similar. The purpose of this Letter is to demonstrate that the I-N transition in $d = 2$ is far more subtle. Our results are inspired by *generalized* XY models in $d = 2$ [7], for which it has been proved that the KT transition can become first-order [8]. Since Eq. (1) can be mapped onto the generalized XY model, using $(\cos x)^{2p} = 2^{-p}(1 + \cos(2x))^p$, the consequences of this result should be relevant for liquid crystals as well. Indeed, for liquid crystals interacting via Eq. (1) with large p, a first-order transition is found, including a phase coexistence region, characterized by a finite line tension. For smaller p, nonuniversal critical behavior is found, with exponent ratios that vary continuously with p, while obeying hyperscaling. Interestingly, the variation of the exponent ratios we observe

is qualitatively similar to that of the $d = 2$ Potts model [9]. Finally, we consider an *off-lattice* liquid crystal, which turns out to also exhibit nonuniversal critical behavior.

We begin our investigation by considering Eq. (1) in the limit of large p, such that the nearest neighbor interaction is "sharp and narrow." In other words, two neighboring molecules lower the energy *only* when they are closely aligned; otherwise, the interaction quickly vanishes, which mimics the Kronecker-δ Hamiltonian of the Potts model [9]. In fact, for large p, Eq. (1) qualitatively resembles the q-state Potts model, with $q \propto p^{1/2}$ [7]. The q-state Potts model in $d = 2$ exhibits a first-order phase transition when $q > 4$, and so one may hope to see a similar transition in Eq. (1) when p becomes large. To this end, we have Monte Carlo simulated Eq. (1) with $p = 1000$, on a periodic $L \times L$ lattice. The simulations are performed using standard single-particle Metropolis moves, combined with a biased sampling scheme [10], and histogram reweighting [11]. Evidence of a first-order transition is obtained from the distribution $P(E)$, defined as the probability to observe the energy E during the simulation [12]. For $\epsilon \approx 2.5$ and $p = 1000$, we find that $P(E)$ becomes bimodal, see Fig. 1(a). The peak at low energy (I) reflects the quasi-nematic phase, the peak at high energy (II) the isotropic phase, and the region in between the peaks corresponds to phase coexistence (the latter is characteristic of first-order transitions). Simulation snapshots obtained in the region where $P(E)$ attains its minimum strikingly confirm phase coexistence, see Fig. 1(b). Here, a rectangular lattice was used, such that the interfaces form parallel to the short edge of the lattice, since this minimizes the total amount of interface in the system. Note that the coexistence is between an isotropic and a quasi-nematic phase: both phases lack long-range order in the thermodynamic limit. The decay of nematic order with system size in the quasi-nematic phase may, however, be very slow, giving the impression of a true nematic phase [13]. The interfaces in Fig. 1(b) are not flat and appear to be decorated with capillary waves. Our results even allow for an estimate of the line tension λ between the coexisting domains. To this end, note that we have plotted the logarithm of $P(E)$ divided by $2L$ in Fig. 1(a), with the minimum between the peaks shifted to zero. The height of the peaks then reflects the line tension [14]. The results of both system sizes are remarkably consistent and yield $\lambda \approx 0.3 k_B T$ per lattice spacing.

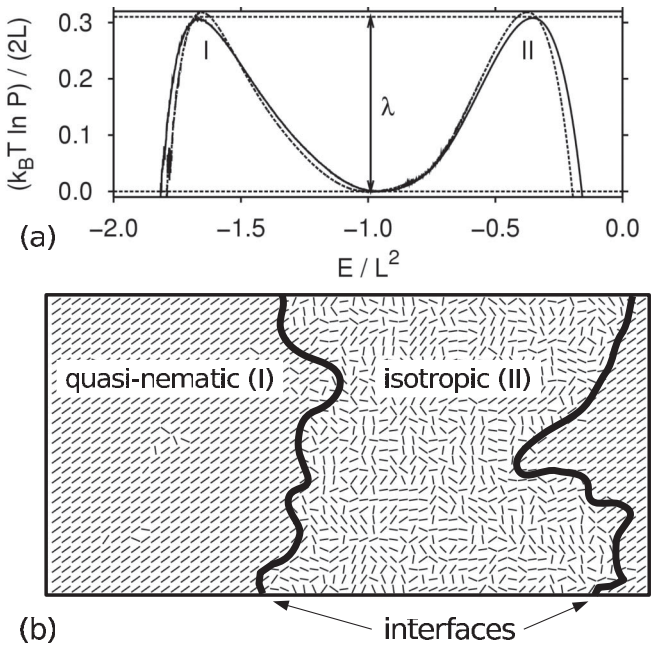

FIG. 1. Evidence of a first-order phase transition in the thermotropic liquid crystal of Eq. (1) with $p = 1000$ at $\epsilon \approx 2.5$. (a) Scaled and shifted logarithm of $P(E)$ for $L = 10$ (solid curve) and $L = 15$ (dashed curve); λ reflects the line tension of the I-N interface. (b) Typical snapshot obtained in the coexistence region.

Next, we investigate what happens when the interaction of Eq. (1) is no longer "sharp and narrow." Clearly, for $p = 2$ in Eq. (1), critical behavior of the XY model should be detected. Therefore, somewhere in the interval $2 < p < 1000$, a crossover to first-order behavior must take place. We have performed additional simulations of Eq. (1), and find that for $p < 50$, bimodal energy distributions $P(E)$ can no longer be identified. In fact, the case $p = 50$ is near the borderline: for small systems, bimodal energy distributions do occur, at $\epsilon \approx 1.86$, but the free energy barrier $\Delta F \equiv 2L\lambda$ decreases with L, and so the bimodal structure does not survive the thermodynamic limit. Following Ref. [15], we conclude that the transition in Eq. (1) is no longer first-order when $p \leq 50$. Interestingly, a similar phenomenon also occurs in the two-dimensional q-state Potts model [9]. Here, $q = 4$ is the borderline case: when $q \leq 4$, the Potts model no longer exhibits a first-order phase transition. Instead, the transition becomes critical, with critical exponents that depend on q. If we accept that p in Eq. (1) is analogous to the number of Potts states q, then $p = 50$ roughly corresponds to $q = 4$. It then becomes of interest to investigate the critical behavior of Eq. (1) in the regime $p \leq 50$. If the analogy to the Potts model remains valid, critical exponents that depend on p are to be expected.

To this end, we now consider Eq. (1) using $p = 10$. Since $P(E)$ is no longer bimodal, a different quantity must be used to locate the phase transition. For liquid crystals, a natural choice is the nematic order parameter S, defined as the maximum eigenvalue of the orientational tensor $Q_{\alpha\beta} = \sum_{i=1}^{N}(2d_{i\alpha}d_{i\beta} - \delta_{\alpha\beta})$, with $d_{i\alpha}$ the α component ($\alpha = x, y$) of the orientation $\vec{d}_i$ of molecule i, $\delta_{\alpha\beta}$ the Kronecker delta, and N the total number of particles. For disordered phases, S will be small; for ordered phases with strong alignment, S will be larger. We simulate Eq. (1) as before, and measure the distribution $P(S)$, defined as the probability to observe the nematic order parameter S. First evidence of a phase transition is provided in Fig. 2(a). Shown is $W \equiv \ln P(S)$ for several values of ϵ. The striking feature of Fig. 2(a) is the formation of a "kink" in W, when

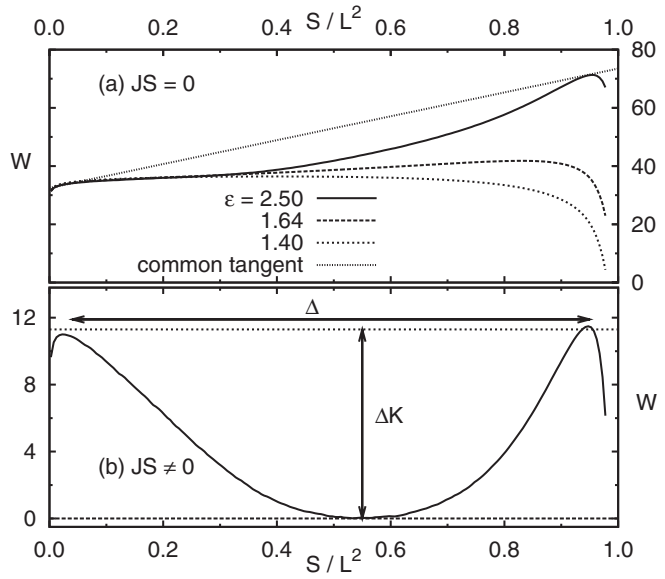

FIG. 2. Nematic order parameter distributions $W \equiv \ln P(S)$ of Eq. (1) for $p = L = 10$. (a) W in the *absence* of JS, for several ϵ, including the "common tangent" construction for $\epsilon = 2.5$. (b) Bimodal form of W for $\epsilon = 2.5$, in the *presence* of JS, including the definition of ΔK and Δ.

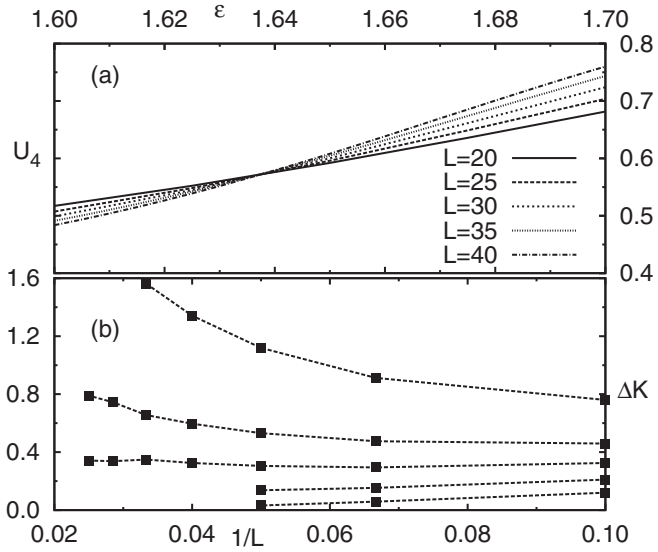

FIG. 3. Finite size scaling analysis of Eq. (1) with $p = 10$. (a) U_4 as a function of ϵ for several system sizes L. The intersection point yields an estimate of ϵ_{cr}. (b) ΔK as a function of $1/L$, for $\epsilon = 1.70$; 1.66; 1.64; 1.62; 1.60 (top to bottom).

ϵ is sufficiently large. It then becomes possible to perform a "common tangent" construction. We thus find a rather special phase transition, characterized by a change in the shape of W. The transition is one from a high-temperature (low ϵ) phase, where "common tangents" in W do not occur, to a low-temperature (high ϵ) phase, where they do. We note in passing that the probability distribution of the magnetization in the two-dimensional XY model shows similar behavior [6]. In other words, the formation of a kink does not imply long-range order in Eq. (1), which indeed is ruled out by the MW theorem [4].

To accurately locate the value of ϵ above which the kink in W begins to form, it is convenient to add a term JS to the Hamiltonian, such that Eq. (1) becomes $\mathcal{H} = -\epsilon \sum_{\langle i,j \rangle} |\vec{d}_i \cdot \vec{d}_j|^p + JS$, with S the nematic order parameter, and coupling constant J. The effect of $J > 0$ is to penalize the nematic phase. Provided a kink is present, W can be cast into bimodal form. Figure 2(b) gives an example for $\epsilon = 2.5$. Here, J was tuned using $P_{J\neq 0}(S) = P_{J=0}(S) \exp(-JS)$, such that the two peaks in $P(S)$ were of equal area [16]. The magnitude of the kink now shows up as a barrier, marked ΔK in Fig. 2(b). To locate the transition, we use the finite size scaling approach of Ref. [15]. To this end, ΔK is measured as a function of ϵ and L. The result is shown in Fig. 3(b). For small ϵ, ΔK decreases with system size, implying that the kink does not survive the thermodynamic limit. For large ϵ, ΔK increases with system size, in which case the kink survives. For intermediate ϵ, ΔK remains roughly constant, implying that the transition from the low-ϵ "kinkless" phase, to the high-ϵ kink phase, passes through a critical point [15], at $\epsilon \approx 1.64$. Further confirmation is obtained from the Binder cumulant $U_4 \equiv \langle m^2 \rangle^2 / \langle m^4 \rangle$ of the bimodal distributions, with $m = S - \langle S \rangle$, see Fig. 3(a). At a critical point, the cumulant becomes L-independent [17]. The sharp intersection point in Fig. 3(a) provides strong evidence that Eq. (1) indeed becomes critical. For $p = 10$, criticality is obtained at $\epsilon_{cr} \approx 1.637$, in excellent agreement with the previous estimate.

Having established the critical value of ϵ, critical exponent ratios can be measured in several ways. For example, β/ν is obtained by fitting the decay of the order parameter Δ at ϵ_{cr} to Eq. (2), with Δ defined in Fig. 2(b). Similarly, γ/ν follows from the finite size behavior of the susceptibility $\chi = (\langle S^2 \rangle - \langle S \rangle^2)/L^2$ at ϵ_{cr}, see Eq. (2). In addition, exponent ratios can be obtained using the method of Loison [18]. We find that both techniques are remarkably consistent: for $p = 10$ in Eq. (1), we obtain $\beta/\nu \approx 0.175$ and $\gamma/\nu \approx 1.645$. Note that these ratios strikingly obey the hyperscaling relation $\gamma/\nu + 2\beta/\nu = d$. By repeating the above analysis for different values of p, the result of Fig. 4 is obtained. Shown are ϵ_{cr} (a), β/ν (b), and γ/ν (c), as a function of p. We first note that the exponent ratios for $p \neq 10$ also obey hyperscaling. This result is important because it demonstrates the consistency of our data and provides additional confirmation that Eq. (1), for small p, indeed becomes critical at the transition point. An even more striking feature is that the exponent ratios depend on p. Such nonuniversal critical behavior may seem surprising, but has been observed before in different systems [19]. Indeed, based on the analogy to the Potts model, p-dependent critical behavior was already anticipated. In fact, the nonmonotonic variation of the exponent ratios we observe in Fig. 4 is also characteristic of the q-state Potts model. In this case, the exponent ratios assume their extrema at $q \approx 3.33$. Our results thus suggest

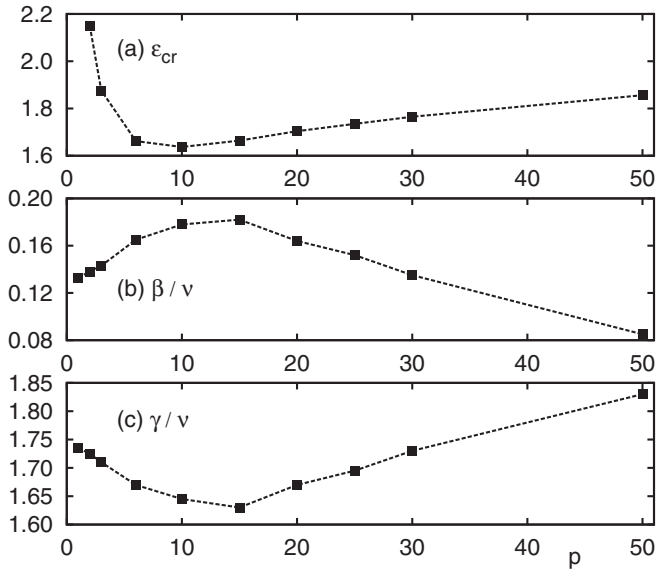

FIG. 4. Critical properties of Eq. (1) as a function of p.

that Eq. (1) for $p \sim 10$–20 roughly corresponds to a $q \sim 3$ Potts model. The actual exponent values of the Potts model, however, do not agree with those of Fig. 4. In other words, the analogy between Eq. (1) and the Potts model is not exact. Note that the rotation symmetry of Eq. (1) is *not* the permutation symmetry of the Potts model. An exact correspondence is therefore not to be expected. This is also manifested by the behavior of ϵ_{cr}, see Fig. 4(a). Whereas the increase of ϵ_{cr} with p for large p is consistent with the Potts model, the decrease at small p is not. In fact, for $p = 2$ in Eq. (1), we expect XY critical behavior to occur. As Fig. 4(c) demonstrates, γ/ν is indeed close to the XY value $7/4$ [3] in that case.

We now consider an off-lattice liquid crystal, namely, a fluid of soft rods. The rods are defined as rectangles, of length l and width w, capped at each end by a semicircle of diameter w (we set $l/w = 16$, and l will be the unit of length). The rods interact via a repulsive pair potential, whereby rod overlap is penalized with energy cost $\kappa = 2$. The rods are simulated in the grand-canonical ensemble, i.e., at constant temperature T, chemical potential μ, and system area A, while the number of particles N fluctuates. We use a simulation square of size $L \times L$, with periodic boundary conditions. While for Eq. (1), a phase transition occurs above a certain ϵ, here that role is played by μ. This also implies that the analogue of energy in Eq. (1) becomes the number of particles N, since μ couples to N in the grand-canonical ensemble. The probability distributions $P(S)$ and $P(N)$ were measured for various μ. We find that bimodal distributions $P(N)$ do *not* occur, strongly suggesting that a first-order transition is absent. In other words, soft rods resemble Eq. (1) in the limit of small p. Indeed, we find that $\ln P(S)$ develops a kink when μ exceeds a critical value μ_{cr}. For $\mu > \mu_{\mathrm{cr}}$, bimodal distributions $\ln P(S)$ can be realized, as in Fig. 2(b), by tuning J. Finite size scaling confirms that the system becomes critical at the point where the kink first appears. For soft rods, $\mu_{\mathrm{cr}} \approx 1.985$, $\beta/\nu \approx 0.17$, and $\gamma/\nu \approx 1.65$ are obtained, consistent with hyperscaling. By comparing to Fig. 4, we conclude that soft rods resemble Eq. (1) with $p \sim 10$–20.

In summary, for a *lattice* liquid crystal with "sharp and narrow" interactions, the existence of a first-order transition was shown, including an estimate of the line tension between the coexisting domains. The line tension is small, giving rise to strong interface fluctuations. When the interaction is no longer "sharp and narrow," the transition becomes continuous. Liquid crystals then show nonuniversal critical behavior, with exponent ratios that depend on the "sharpness" of the interaction, but that do obey hyperscaling. In addition, the behavior of the exponent ratios follows the Potts trend. For *lattice* liquid crystals, the transition type can be selected using the parameter p in Eq. (1). For *off-lattice* systems, such a parameter is not so easily identified. In soft rods, the interaction is clearly not "sharp and narrow" enough to induce a first-order transition. It remains of interest to identify *off-lattice* interactions that do facilitate first-order transitions in two-dimensional liquid crystals. Possibly, this could be achieved using Gay-Berne type potentials [20]. A different application could be to use the present simulation methodology to study melting in two dimensions. Such investigations are a topic for future work.

This work was supported by the *Deutsche Forschungsgemeinschaft* under the SFB-TR6/D3. I thank H. Wensink, H. Löwen, A. van Enter, K. Binder, and D. Frenkel for stimulating discussions.

[1] P. Lebwohl and G. Lasher, Phys. Rev. A **6**, 426 (1972).
[2] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).
[3] J. Kosterlitz, J. Phys. C **7**, 1046 (1974).
[4] N. Mermin and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966); P. Bruno, Phys. Rev. Lett. **87**, 137203 (2001).
[5] J. Kosterlitz and D. Thouless, J. Phys. C **6**, 1181 (1973).
[6] P. Archambault *et al.*, J. Phys. A **30**, 8363 (1997).
[7] H. Blöte *et al.*, Phys. Rev. Lett. **52**, 1535 (1984).
[8] A. van Enter and S. Shlosman, Phys. Rev. Lett. **89**, 285702 (2002); Commun. Math. Phys. **255**, 21 (2005).
[9] F. Wu, Rev. Mod. Phys. **54**, 235 (1982).
[10] P. Virnau and M. Müller, J. Chem. Phys. **120**, 10925 (2004).
[11] A. Ferrenberg and R. Swendsen, Phys. Rev. Lett. **63**, 1195 (1989).
[12] A. Billoire *et al.*, Nucl. Phys. B **413**, 795 (1994).
[13] S. Bramwell and P. Holdsworth, J. Phys. Condens. Matter **5**, L53 (1993).
[14] K. Binder, Phys. Rev. A **25**, 1699 (1982).
[15] J. Lee and J. Kosterlitz, Phys. Rev. Lett. **65**, 137 (1990).
[16] K. Binder and D. Landau, Phys. Rev. B **30**, 1477 (1984).
[17] K. Binder, Z. Phys. B **43**, 119 (1981).
[18] D. Loison, J. Phys. Condens. Matter **11**, L401 (1999).
[19] J. Lee *et al.*, Phys. Rev. B **44**, 4819 (1991); B. Nienhuis *et al.*, Phys. Rev. Lett. **43**, 737 (1979).
[20] J. Gay and B. Berne, J. Chem. Phys. **74**, 3316 (1981).