Determination of the critical exponents for the isotropic-nematic phase transition in a system of long rods on two-dimensional lattices: Universality of the transition

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Abstract – Monte Carlo simulations and finite-size scaling analysis have been carried out to study the critical behavior and universality for the isotropic-nematic phase transition in a system of long straight rigid rods of length $k$ ($k$-mers) on two-dimensional lattices. The nematic phase, characterized by a big domain of parallel $k$-mers, is separated from the isotropic state by a continuous transition occurring at a finite density. The determination of the critical exponents, along with the behavior of Binder cumulants, indicate that the transition belongs to the 2D Ising universality class for square lattices and to the three-state Potts universality class for triangular lattices.

Introduction. – The study of systems of large particles in solution is one of the central problems in statistical mechanics and has been attracting a great deal of interest since long ago. Onsager [1] predicted that very long and thin rods interacting with only excluded-volume interaction can lead to long-range orientational (nematic) order. The nematic phase, characterized by a big domain of parallel molecules, is separated from an isotropic state by a phase transition occurring at a finite critical density. Computer simulations of hard ellipses of finite length [2] confirmed Onsager’s classic prediction that particle shape anisotropy can be a sufficient condition to induce the long-range orientational order found in nematic liquid crystals.

Flory [3] and Huggins [4] studied a system of long rod-like molecules by means of a lattice calculation. The approach, which is a direct generalization of the theory of binary liquids in two dimensions, indicates that the lattice model would also show an isotropic-nematic (I-N) phase transition as a function of density.

A notable feature is that nematic order is only stable for sufficiently large aspect ratios while isotropic systems of short rods do not show nematic order at all. The long-range orientational order also disappears in the case of irreversible adsorption (no desorption) [5], where the distribution of adsorbed objects is different from that obtained at equilibrium [6,7]. Thus, at high coverage, the equilibrium state corresponds to a nematic phase with long-range correlations, whereas the final state generated by irreversible adsorption is a disordered state (known as jamming state), in which no more objects can be deposited due to the absence of free space of appropriate size and shape (the jamming state has infinite memory of the process and the orientational order is purely local). Another important factor in the phase stability of long rods is the flexibility of the adparticles. This property plays an important role in systems of, e.g., stiff polymers and linear micelles and its generic effect is a significant depression of the nematic order compared to rigid particles [8].

For the continuum problem, there is general agreement that in three dimensions, infinitely thin rods undergo a first-order I-N transition, as was pointed out by Onsager [1]. In two dimensions, the nature of the I-N transition depends crucially on the particle interactions and a rich variety of behaviors is observed [9,10].

In the case of lattice models of straight hard rods of length $k$, which is the topic of this paper, the inherent complexity of the system still represents a major difficulty to the development of approximate solutions, and computer simulations appear as a very important tool.

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for investigating this subject. In this sense, a system of straight rigid rods of length $k$ on a square lattice, with two allowed orientations, was recently studied by Monte Carlo simulations [11]. Ghosh and Dhar found strong numerical evidence that the system shows nematic order at intermediate densities for $k \geq 7$. However, these authors were not able to determine the critical quantities (critical point and critical exponents) characterizing the I-N phase transition occurring in the system.

Despite these recent results there is a remaining question to be answered: “What type of phase transition is it?”

The objective of this letter is to provide a thorough study in this direction. For this purpose, extensive Monte Carlo (MC) simulations supplemented by analysis using finite-size scaling (FSS) theory [12–14] have been carried out to study the critical behavior in a system of long rigid rods deposited on square and triangular lattices. In the case of FSS analysis, the conventional normalized scaling variable $\epsilon \equiv T/T_c - 1$ was replaced by $\epsilon \equiv \theta/\theta_c - 1$, where $T$, $T_c$, $\theta$ and $\theta_c$ represent temperature, critical temperature, density and critical density, respectively. A nematic phase, characterized by a big domain of parallel $k$-mers, is separated from the disordered state by a continuous phase transition occurring at a finite critical temperature. Based on the strong axial anisotropy of the nematic phase, an order parameter measuring the orientation of the particles has been introduced. Taking advantage of its definition, we were able to study for the first time the universality class of the I-N phase transition occurring in the system. The accurate determination of the critical exponents, along with the behavior of Binder cumulants, confirmed that the transition of rigid rods on square (triangular) lattices, with two (three) allowed orientations, belongs to the 2D Ising (three-state Potts) universality class.

**Model and Monte Carlo method.** – As in ref. [11], we address the general case of adsorbates assumed to be linear rigid particles containing $k$ identical units ($k$-mers), with each one occupying a lattice site. Small adsorbates would correspond to the monomer limit ($k = 1$). The distance between $k$-mer units is assumed to be equal to the lattice constant; hence exactly $k$ sites are occupied by a $k$-mer when adsorbed. The only interaction between different rods is hard-core exclusion: no site can be occupied by more than one $k$-mer. The surface is represented as an array of $M = L \times L$ adsorptive sites in a square or triangular lattice arrangement, where $L$ denotes the linear size of the array.

The degree of order in the adsorbed phase is calculated for each configuration according to the standard method used for the Potts model [15]. To this end, we first build a set of vectors $\{\vec{v}_1, \vec{v}_2, \ldots, \vec{v}_n\}$ with the following properties: i) each vector is associated to one of the $n$ possible orientations (or directions) for a $k$-mer on the lattice; ii) the $\vec{v}_i$’s lie in a two-dimensional space (or are co-planar) and point radially outward from a given point $P$ which is defined as coordinate origin; iii) the angle between two consecutive vectors, $\vec{v}_i$ and $\vec{v}_{i+1}$, is equal to $2\pi/n$; and iv) the magnitude of $\vec{v}_i$ is equal to the number of $k$-mers aligned along the $i$-direction. Note that the $\vec{v}_i$’s have the same directions as the $q$ vectors in ref. [15]. These directions are not coincident with the allowed directions for the $k$-mers on the real lattice. Then the order parameter $\delta$ of the system is given by

$$
\delta = \frac{\sum_{i=1}^{n} |\vec{v}_i|}{\sum_{i=1}^{n} |\vec{v}_i|}.
$$

(1)

$\delta$ represents a general order parameter measuring the orientation of the $k$-mers on a lattice with $n$ directions. In

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Even though it is theoretically expected that the I-N transition in a system of long rigid rods on a square (triangular) lattice belongs to the 2D Ising (three-state Potts) universality class [11], numerical verification of this has not been possible so far.
the case of square lattices, \( n = 2 \) and the angle between \( \vec{v}_1 \) and \( \vec{v}_2 \) is \( \pi \) (see fig. 1(a)). Accordingly, the order parameter reduces to \( \delta = |v_1 - v_2| / (v_1 + v_2) \), \( v_1 (v_2) \) being the number of \( k \)-mers aligned along the horizontal (vertical) direction. This expression coincides with the order parameter \( Q \) defined in ref. [11]. On the other hand, \( n = 3 \) for triangular lattices and \( \vec{v}_1, \vec{v}_2 \) and \( \vec{v}_3 \) form angles of \( 2\pi/3 \) between them (see fig. 1(b)).

When the system is disordered (\( \theta < \theta_c \)), all orientations are equivalent and \( \delta \) is zero. As the density is increased above \( \theta_c \), the \( k \)-mers align along one direction and \( \delta \) is different from zero. Thus, \( \delta \) appears as a proper order parameter to elucidate the phase transition.

The problem has been studied by grand canonical Monte Carlo simulations using an adsorption-desorption algorithm. The procedure is as follows. At each time step, a linear \( k \)-uple of nearest-neighbor sites is chosen at random. Then, if the \( k \) sites are empty, an attempt is made to deposit a rod with probability \( p \); if the \( k \) sites are occupied by units belonging to the same \( k \)-mer, an attempt is made to desorb this \( k \)-mer with probability \( 1 - p \); and otherwise, the attempt is rejected. A Monte Carlo step (MCS) is achieved when \( M \) \( k \)-uples of sites have been tested to change its occupancy state. Typically, the equilibrium state can be well reproduced after discarding the first \( 10^6 \) MCSs. Then, the next \( 3 \times 10^8 \) MCSs are used to compute averages.

In our Monte Carlo simulations, we varied the adsorption probability \( p \) and monitored the density \( \theta \) and the order parameter \( \delta \), which can be calculated as simple averages. The quantities related with the order parameter, such as the susceptibility \( \chi \), and the reduced fourth-order cumulant \( U_L \) introduced by Binder [13] were calculated as

\[
\chi = \frac{L^2}{k_B T} \langle (\delta^2)^2 \rangle - \langle \delta^2 \rangle^2 \quad (2)
\]

and

\[
U_L = 1 - \frac{\langle \delta^4 \rangle}{3 \langle \delta^2 \rangle^2}, \quad (3)
\]

where \( \langle \cdots \rangle \) means the average over the MC simulation runs. All calculations were carried out using the BACO parallel cluster (composed by 60 PCs each with a 3.0 GHz Pentium-4 processor) located at Laboratorio de Ciencias de Superficies y Medios Porosos, Universidad Nacional de San Luis, San Luis, Argentina. The total CPU time for the present study is estimated of about 900 days on one node of the BACO cluster.

**Results.** – The critical behavior of the present model has been investigated by means of the computational scheme described in the previous paragraphs and of finite-size scaling analysis. The FSS theory implies the following behavior of \( \delta, \chi \) and \( U_L \) at criticality:

\[
\delta = L^{-\beta/\nu} \tilde{\delta}(L^{1/\nu} \epsilon), \quad (4)
\]

\[
\chi = L^{\gamma/\nu} \tilde{\chi}(L^{1/\nu} \epsilon) \quad (5)
\]

and

\[
U_L = \tilde{U}_L(L^{1/\nu} \epsilon), \quad (6)
\]

for \( L \to \infty, \epsilon \to 0 \) such that \( L^{1/\nu} \epsilon = \text{finite} \). Here \( \beta, \gamma, \) and \( \nu \) are the standard critical exponents of the order parameter \( \delta \sim -\epsilon^{\beta} \) for \( \epsilon \to 0^- \), \( L \to \infty \), susceptibility \( \chi \sim |\epsilon|^{\gamma} \) for \( \epsilon \to 0 \), \( L \to \infty \) and correlation length \( \xi \) \( \xi \sim |\epsilon|^{-\nu} \) for \( \epsilon \to 0 \), \( L \to \infty \), respectively. \( \delta, \chi \) and \( U_L \) are scaling functions for the respective quantities.

In the case of conventional FSS theory, when the phase transition is temperature driven, \( \epsilon \equiv T/T_c - 1 \). In our study, we modified the standard FSS analysis by replacing temperature by density. Under this condition, \( \epsilon \equiv \theta/\theta_c - 1 \).

The calculations were developed for linear 10-mers \( (k = 10) \). With this value of \( k \), the existence of a nematic phase at intermediate densities is expected. The surface was represented as an array of adsorptive sites in a square or triangular lattice arrangement. In addition, conventional periodic boundary conditions were considered. The effect of finite size was investigated by examining square lattices with \( L = 50, 100, 150, 200 \) and triangular lattices with \( L = 100, 150, 200, 250 \), with an effort reaching almost the limits of our computational capabilities.

The critical density has been estimated from the plots of the reduced fourth-order cumulants \( U_L(\theta) \) plotted vs. \( \theta \) for several lattice sizes. In the vicinity of the critical point, cumulants show a strong dependence on the system size. However, at the critical point the cumulants adopt a nontrivial value \( U^* \), irrespective of system sizes in the scaling limit. Thus, plotting \( U_L(\theta) \) for different linear

![Fig. 2: Curves of \( U_L(\theta) \) vs. \( \theta \) for square lattices of different sizes: squares, \( L = 50 \); circles, \( L = 100 \); triangles, \( L = 150 \); and diamonds, \( L = 200 \). From their intersections one obtains \( \theta_c \). The inset in the upper-left (lower-right) corner shows a typical configuration in the isotropic (nematic) phase.](image-url)
Fig. 3: (a) Data collapsing, $U_L$ vs. $\varepsilon L^{1/\nu}$, for the cumulants in fig. 2. In the inset, the data in fig. 2 are plotted over a wide range of coverage. (b) Data collapsing of the order parameter, $\delta L^{\beta/\nu}$ vs. $|\varepsilon| L^{1/\nu}$, and of the susceptibility, $\chi L^{\gamma/\nu}$ vs. $\varepsilon L^{1/\nu}$ (inset). The plots were made using $\theta_c = 0.502$ and the exact 2D Ising exponents $\nu = 1$, $\beta = 0.125$ and $\gamma = 1.75$.

Fig. 4: (a) Data collapsing of the cumulants for triangular lattices. The corresponding curves of $U_L(\theta)$ vs. $\theta$ are shown in the inset. (b) Same as fig. 3(b) for triangular lattices. The plots were made using $\theta_c = 0.530$ and the exact three-state Potts model exponents $\nu = 5/6$, $\beta = 1/9$ and $\gamma = 13/9$.

dimensions yields an intersection point $U^*$, which gives an accurate estimation of the critical density in the infinite system. Figure 2 shows this procedure for square lattices. The value obtained for the critical density was $\theta_c = 0.502(1)$. In addition, the fixed value of the cumulants, $U^* = 0.615(5)$, is consistent with the extremely precise transfer matrix calculation of $U^* = 0.6106901(5)$ [16] for the 2D Ising model. This finding may be taken as a first indication of universality. However, as recently pointed out by Selke et al. [17,18], the value of the cumulant intersection may depend on various details of the model, which do not affect the universality class, in particular, the boundary condition, the shape of the lattice, and the anisotropy of the interactions. Consequently, more research is required to determine the universality class of a phase transition.

Once we know $\theta_c$, the critical exponent $\nu$ can be calculated from the full data collapsing of $U_L$. The results are shown in fig. 3(a), where an excellent fit was obtained for $\nu = 1$. In the inset, the data are plotted over a wider range of temperatures, exhibiting the typical behavior of the cumulants in the presence of a continuous phase transition.

Given $\theta_c = 0.502(1)$ and $\nu = 1$, $\beta$ and $\gamma$ were obtained from the collapse of the curves of $\delta$ and $\chi$, as is shown in fig. 3(b). The data scaled extremely well using $\beta = 1/8$ and $\gamma = 7/4$. The results in figs. 2 and 3 support the hypothesis of 2D Ising universality class, which is consistent with the two competing ordered states near the transition.

We now analyze the results corresponding to triangular lattices. In this case, there are three competing ordered states (the order parameter has three components) and
this transition is expected to be in the universality class of the two-dimensional Potts model with $q = 3$. The inset in fig. 4(a) shows Binder cumulants plotted vs. $\theta$. The intersection point converges to a fixed point, allowing an accurate estimation of the critical density ($\theta_c = 0.530(1)$) and of the fixed value of the cumulants ($U^* = 0.613(5)$). This value of $U^*$ is practically indistinguishable from previous estimates for the three-state Potts model (see, for instance, ref. [19], where $U^* \approx 0.613$).

On the other hand, the critical exponents were obtained from the scaling plots of $U_L$ (fig. 4(a)), $\delta$ (fig. 4(b)) and $\chi$ (inset in fig. 4(b)). Very good collapses were obtained using the exact 2D three-state Potts model scaling parameters ($\nu = 5/6$, $\beta = 1/9$ and $\gamma = 13/9$). Our findings are consistent with the hypothesis that this phase transition, occurring on triangular lattices, belongs to the universality class of the two-dimensional Potts model with $q = 3$.

In summary, we have used Monte Carlo simulations and finite-size scaling theory to resolve the universality class of the I-N phase transition occurring in a system of long rods on square lattices with two allowed orientations and triangular lattices with three allowed orientations. As was evident from the calculation of the critical exponents and the behavior of Binder cumulants, the universality class was shown to be that of the 2D Ising model for square lattices and that of the 2D Potts model with $q = 3$ for triangular lattices.

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