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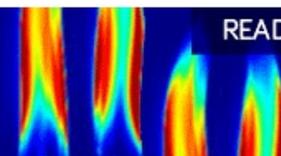
Ordering of rods near planar and curved surfaces

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We study the orientational profile of a semi-infinite system of cylinders bounded in two different ways: by a flat and by a curved wall. The latter corresponds to the interior of a spherical shell, where the dimensions of the rods are comparable to the radius of curvature of the container: they have to accomodate to fill the available space, leading to a rich orientation profile. In order to study these problems, we make a mapping onto a three-state Potts model on a semi-infinite lattice, which is solved using a mean-field approach; we fix the boundary conditions on the surface and in the bulk. In the case of a curved surface, the increase in the effective volume interactions towards the bulk, due to compression, is obtained by increasing the nearest neighbor interactions. The mean-field equations are iterated numerically and we obtain various interesting results concerning the free energy and the orientation profile. We show that there is always a first order transition and the stability of the coexisting phases is strongly affected by the surface. When the surface is disordered and the bulk ordered, the profile may present a step that depends on the degree of disorder on the surface, on the rate of increase of the particle interactions and on the surface external potential. The existence of this step may be relevant to applications in nanotechnology. © *2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5013233

I. INTRODUCTION

Understanding surface effects in liquid crystals has attracted a great deal of attention for a long time, very often motivated by industrial applications. Examples are the first twisted nematic displays cells,[1] where the effects of confinement is a crucial issue; later on, attention has turned to light-shutter devices based on polymer dispersed liquid crystals,[2] which motivated the study of confinement in spherical geometries. In these systems the size of the particles is irrelevant: typically, the confining volumes are of the order of micrometers, much larger than the particle sizes, of a few nanometers; in this situation the description by means of continuum theories[3] is plenty satisfactory.

More recently, attention has turned to macroscopic liquid crystals formed by viruses,[4,5] filamentous biopolymers[6] and carbon nanotubes,[7,8] however the organization of such colloidal liquid crystals in spherical droplets is yet a largely unexplored area of research. On the theoretical point of view, the main obstacle for their description is the larger size of the particles: they range from a tenth to a few micrometers, being comparable to the container dimensions, so that continuum theories break down. The general problem consists in understanding how colloidal particles accomodate to find their optimal conformation when mutual packing and alignment to boundaries compete at the same length scale. Some theoretical descriptions have addressed such problems

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using Monte Carlo simulations[9–12] and a combination of Monte Carlo simulations and molecular dynamics.[13]

Our problem consists of a colloidal liquid crystal represented by a system of rod-like particles. The main goal is to describe the orientation of these rods inside a curved surface in the regime were excluded volume interactions drive the ordering. For a given concentration, this occurs when the rod dimensions are large enough with respect to the surface curvature radius; this condition will become more precise in the next section. We follow Oliveira and Figueiredo Neto[14] and associate the orientation of each rod to a microscopic state of the three-state Potts model and solve it on a lattice.

We thus have a three-dimensional lattice bounded by a spherical shell. Our first hypothesis is that we can treat such a structure as a set of independent parallel disks, for we are looking for the rods orientational profile of each disk. Our second hypothesis is that, in a given disk, every row contains the same number of rods. The orientation profile of a given disk can be understood as follows: (i) next to the circumference there is enough room to accomodate a given number of particles, anchored in a specific way; (ii) above the circumference, in the upper rows, less room is available which amounts to an increase in the nearest neighbor excluded volume interactions and an enhancement in the row ordering; (iii) for rows closer to the center of the disk, the "squeezing" factor becomes so strong that there is not enough room to accomodate the same number of rods as in the lower rows for they almost touch each other: some particles will have to be displaced to neighboring rows with the onset of an isotropic configuration. Here we study regions (i) and (ii).

This paper is organized as follows: in section (II) we define the problem, set the boundaries and describe the mean field version of the three-state Potts model used here; in section (III) we present the results for a simpler problem, the planar surface case and then turn to the curved surface case; we discuss the results in section (IV) and leave the conclusions for session (V).

II. THE PROBLEM

A. The problem boundaries

We model the colloidal liquid crystal as a system of rods on a three-dimensional lattice.

In the planar surface case (PS), a cubic lattice is assembled as a set of parallel planes perpendicular to a common surface. Every plane has an infinite number of rows. In each row, there are N occupied lattice sites (corresponding to N columns).

In the curved surface case (CS), a sphere is formed by a set $\{n\}$ of parallel disks of radii $\{R_n\}$. Each of the disks contains a deformed rectangular lattice, as shown in Fig. 1. On a nth generic disk
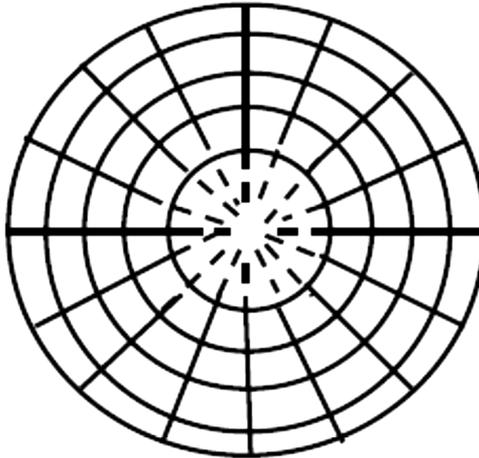

FIG. 1. Network of lattice sites on a given disk next to its circumference.

there are N_n occupied sites in each row (corresponding to N_n "columns"). Such a structure is not well defined near the center of the disks, but our problem does not concern this region.

Each rod has cross section area b^2 and length L ($b < L$). Its geometric center is fixed on a lattice site and it is allowed to rotate freely. The distance between adjacent rows on the same plane (PS) or on the same disk (CS) is larger than $L/2$, the same happens with the distance between adjacent planes or disks. Therefore only nearest neighbors rods in the same row (of a given plane or disk) may constrain the alignment of a given rod.

Next we set the boundaries of the regions of interest. In the PS geometry, there is no "squeezing" effect: the distance between neighboring sites is constant as one moves away from the surface, therefore the excluded volume effect is the same throughout each plane: the region of interest is bounded only by the surface. In the CS case, the boundaries on a nth disk of radius R_n are determined as follows. We suppose the anchoring is homeotropic, and according to our model, the projected excluded volume is bL. We suppose that the circumference can accomodate randomly oriented rods (in the sense described in the above paragraph), this means that $R_n/N_n > L$; nevertheless at a smaller distance $\bar{r}_n$ from the center, the distance between sites in the same row hinders rotation, and this occurs at $\bar{r}_n/N_n \simeq b$. A strong orientational effect sets in between R_n and $\bar{r}_n$ due to the increasing excluded volume interaction. Beyond $\bar{r}_n$ there is no more room to fit all the N_n rods on the same row and an isotropic phase sets in. Therefore for a generic n^{th} disk, the region of interest is: $R_n > r_n > N_n b$.

B. The three-state Potts model

We consider a given plane (or disk) and use the mapping proposed by Oliveira and Figueiredo Neto.[14]

In order to describe the macroscopic order in each row and define a set of order parameters. The orientation of each rod refers to the surface director; for the PS case the surface is flat, for the CS case the surface is the spherical shell. We use the three-state Potts model to describe the system as follows. One of the three states corresponds to alignment perpendicular to the surface (homeotropic), whereas the other two are degenerate and refer to the other orthogonal directions that are parallel to the surface (planar).

We choose an order parameter that describes the mean orientation perpendicular to the surface. Consider a rod on row ℓ: let $\mathbf{\Lambda}_\ell$ be its averaged moment of quadrupole with respect to homeotropic alignment in the rod frame of Ref. 15:

$$\mathbf{\Lambda}_\ell = \begin{bmatrix} -s_\ell/2 & 0 & 0 \\ 0 & -s_\ell/2 & 0 \\ 0 & 0 & s_\ell \end{bmatrix}. \tag{1}$$

The state of ordering is thus described by the set $\{s_\ell\}$.

Because we are interested on the orientation profile in a given plane (or disk), we assume that interactions between rods in different planes (or disks) can be disregarded: the main consequence is the reduction of the $\{s_\ell\}$ by a common multiplicative factor. This is certainly true for the planes and is a good approximation for disks of large radii.

In a mean-field description of the three-state Potts model,[16] the expression for the energy per column of a given plane (or disk) is given by

$$\mathsf{F} = \sum_{\ell=0}^{\infty} \mu_\ell s_l - \sum_{\ell=0}^{\infty} \epsilon_\ell s_\ell s_{\ell+1} - \sum_{\ell=0}^{\infty} \epsilon_\ell (s_\ell)^2$$
$$+ \frac{k_B T}{3} \sum_{\ell=0}^{\infty} [2(1 - s_\ell) \ln(1 - s_\ell) + (1 + 2s_\ell) \ln(1 + 2s_\ell) - 3 \ln 3], \tag{2}$$

The index ℓ labels the rows: $\ell = 1$ refers to the first row, next to the lower boundary (surface): a line on a flat surface (PS) or a circumference (CS); $\ell = \infty$ corresponds to the bulk. The role of s_0 is to fix the anchoring condition as specified below. Each site has two nearest neighbors in the same row and one nearest neighbor in the row just above it. μ_ℓ is the external potential on layer ℓ; ϵ_ℓ is the

interaction energy between a rod in row ℓ and its nearest neighbors in the same row, the interaction energy between nearest neighbors rods in rows ℓ and $\ell + 1$ is also ϵ_ℓ.

Following the general procedure of the mean field approach, we minimize the expression above with respect to s_ℓ to obtain the recurrence relation:

$$s_\ell = \frac{\mu_\ell}{2\epsilon_\ell} - \frac{1}{2}(s_{\ell+1} + s_{\ell-1}) + \frac{k_B T}{3\epsilon_\ell} \ln \frac{1 + 2s_\ell}{1 - s_\ell}. \tag{3}$$

This recurrence relation is solved numerically, under two constraints as follows.

The first, refers to the mean orientation in the bulk, s_∞, which is obtained from equation (3), by fixing $s_\ell = s_{\ell+1} = s_{\ell-1}$:

$$s_\infty = \frac{k_B T}{6\epsilon_\infty} \ln \frac{1 + 2s_\infty}{1 - s_\infty} \tag{4}$$

The second, concerns the anchoring condition on the surface, specified by s_0. Stability requires

$$\frac{1 + 2s_\ell}{1 - s_\ell} > 0, \tag{5}$$

obtained from equation (3). For any s_ℓ, the above condition gives $-1/2 < s_\ell < 1$, according to equation (1); the upper and lower bounds for s_0 correspond to complete homeotropic and complete planar anchoring states respectively, while $s_0 = 0$ is associated to a disordered surface.

Interactions between the surface and the rods are short ranged and are described by an external potential just on the first row.

The orientation of the rods in the vicinity of the surface is driven both by the anchoring value s_0 and by this additional μ_1. In most cases μ_1 is set equal to zero for s_0 is enough to account for the surface orientational effect.

III. NUMERICAL PROCEDURE AND RESULTS

We iterate the equations presented above; in most cases, 300 layers are enough to reach the bulk value asymptotically. In what follows we use reduced parameters: the non-dimensional temperature $\theta = k_B T/\epsilon$ and chemical potential $a_1 = \mu_1/\epsilon$. We start by presenting the results for the PS case and then turn to the CS case.

A. The planar surface (PS) case

In this case, the overall profile is determined by the bulk value, whereas the anchoring condition $s(0)$ affects only the region next to the surface; this is illustrated in Fig. 2.
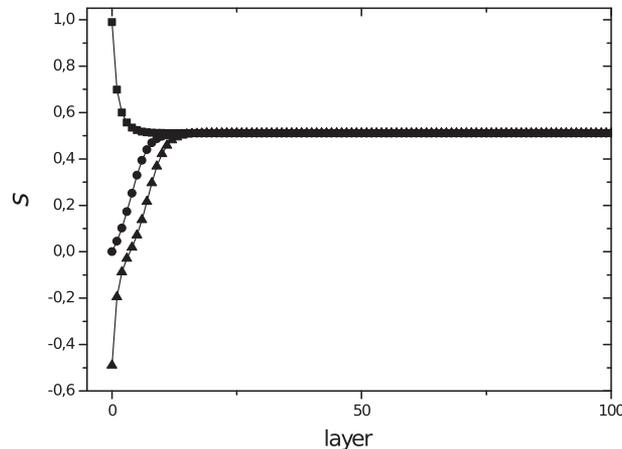

FIG. 2. PS case. Dependence of the profile on anchoring. Filled triangles: $s(0) = -0.49$; filled circles: $s(0) = 0.00$ and filled squares: $s(0) = 0.99$ (joining lines are just guides to the eye). $\theta = 2.16$ and $a_1 = 0$.
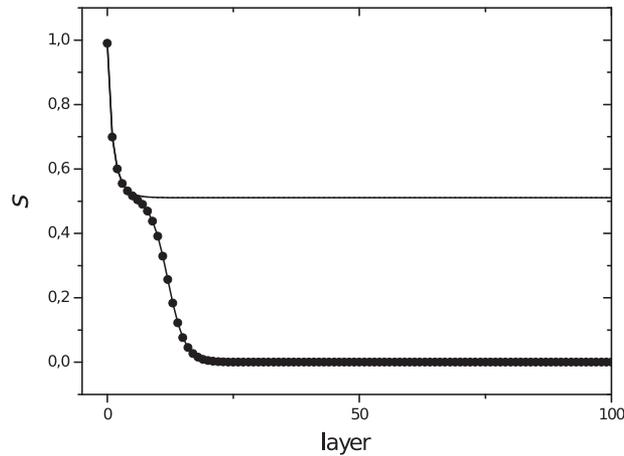
FIG. 3. PS case. Order parameter profile for $\theta = 2.16$. Continuous line: ordered solution; dots on joining line (just a guide to the eye): disordered solution. $s(0) = 0.99$ and $a_1 = 0$.

The existence of a first order transition is well known in analogous three-dimensional systems. In the presence of a surface, the first order phase transition is illustrated in Fig. 3 and in Fig. 4. Fig. 3 shows the order parameter profile at $\theta = 2.16$, in the coexistence domain; Figs. 4 show the evolution of free energy averaged over an increasing number of rows. Fig. 4-I is a comparison between the mean free energy of the first 20 rows next to the surface and the bulk solution, Fig. 4-II compares the first 50 rows and the bulk and Fig. 4-III compares the first 100 rows and the bulk. They show that the bulk behavior, concerning free energy and transition temperature, is reached asymptotically with increasing number of rows. The most interesting feature is observed in the coexistence region: in Fig. 4-I (average over 20 layers) the ordered solution is the only stable solution, increasing the number of rows, a region where the disordered configuration is the stable solution starts to appear (Figs. 4-II and 4-III). We checked that these results are independent of the anchoring value.

The external potential applied to the first row has no effect on the overall profile: in a few rows the system stabilizes to its value in the bulk; this is shown in Fig. 5, where the profile corresponds to a sufficiently low θ so that the system is ordered in the bulk.

By comparing Fig. 2 and Fig. 5 we notice that the anchoring condition and the external potential applied to the first row produce qualitatively the same effect on the profile.

B. The curved surface (CS) case

Here we show the results for increasing interactions towards the bulk. The same as in the PS case, the anchoring condition affects the profile just next to the surface, the overall profile and the system free energy are independent of the anchoring value (not shown here).

We start comparing the full mean free energy (all rows) and the bulk free energy as a function of the bulk reduced temperature θ_∞, illustrated in Fig. 6; in this case we consider only the mean over all rows because the system evolves all the way until the bulk. We notice that the mean free energy is always higher than the bulk free energy; the coexistence region shows a stable ordered and a stable disordered phase and the transition occurs at approximately the same point as in the bulk case.

Fixing low values for the interactions near the surface (high θ_1's) we obtain a disordered configuration there. In order to study how order is reached towards the bulk, we consider two different interaction increase rates (θ's decrease rates), shown in Fig. 7: $\epsilon_\ell \sim \ell$ and $\epsilon_\ell \sim \ell^{0.7}$. For a disordered bulk, the profile of both curves coincide and the result is trivial (not shown here); for an ordered bulk, the order parameter profile reaches the bulk value and it may present a step corresponding to a disordered region: its width increases as the increase rate of ϵ_ℓ becomes smoother.

The dependence of ϵ_ℓ with ℓ characterizes the alignment strength of the excluded volume interactions. Suppose we have a fixed surface curvature radius R; let d_ℓ be the distance between neighboring
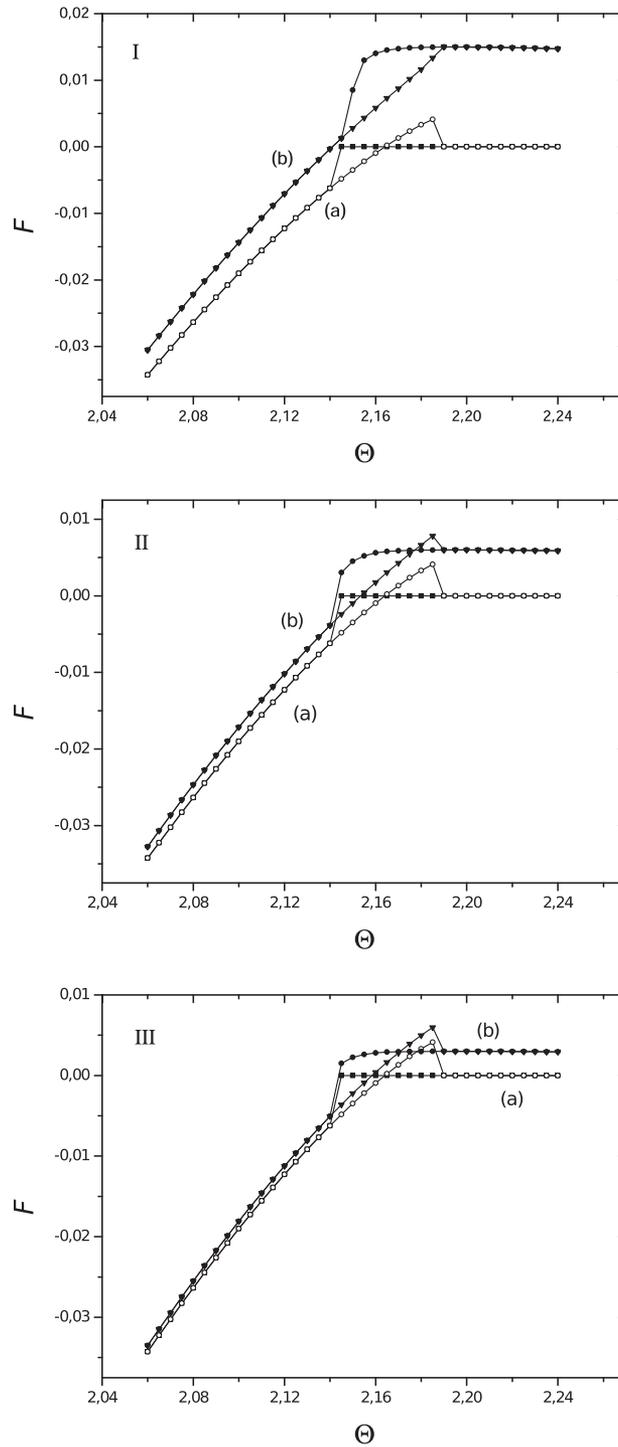
FIG. 4. PS case. Subsystem free energy (b) compared to the bulk free energy (a) as a function of the reduced temperature. (I) first 20 rows; (II) first 50 rows and (III) first 100 rows. Open circles: ordered bulk; filled squares: disordered bulk; filled triangles: ordered subsystem and filled circles: disordered subsystem. $s(0) = 0.99$ and $a_1 = 0$.

rods on row ℓ and a the lattice parameter. Then $(R - \ell.a)/N \simeq d_\ell$ or $(1 - a.\ell/R) \sim d_\ell$. If $\epsilon \sim \ell^\gamma$, where γ is a generic exponent, then $\epsilon \sim (1 - d_\ell)^\gamma$. This means that the alignment strength ϵ depends on the distance between rods d like $(1 - d)^\gamma$.
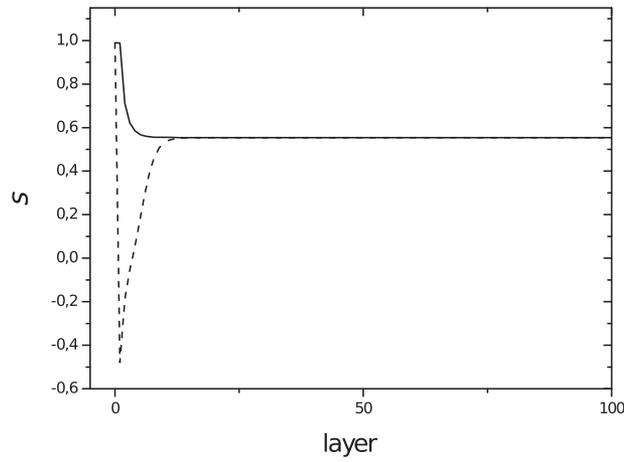
FIG. 5. PS case. Dependence of the profile on the external potential for $\theta = 2.14$. Continuous curve: $a_1 = -5.0$; dashed curve: $a_1 = +5.0$. $s(0) = 0.99$.
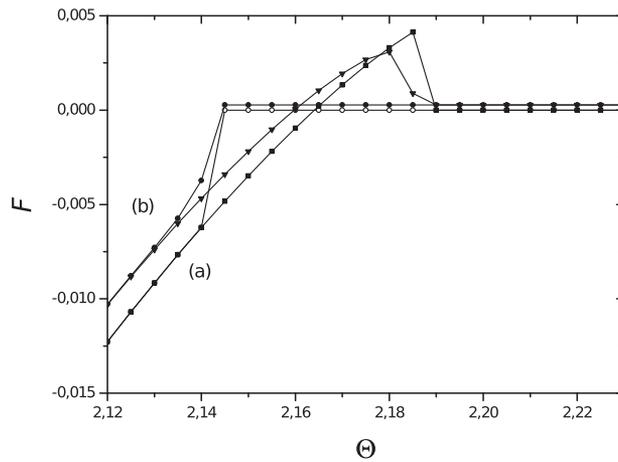

FIG. 6. CS case. System free energy (b) compared to the bulk free energy (a) as a function of the bulk reduced temperature. Open circles: ordered bulk; filled squares: disordered bulk; filled triangles: ordered system and filled circles: disordered system. $s(0) = 0.99$ and $a_1 = 0$.
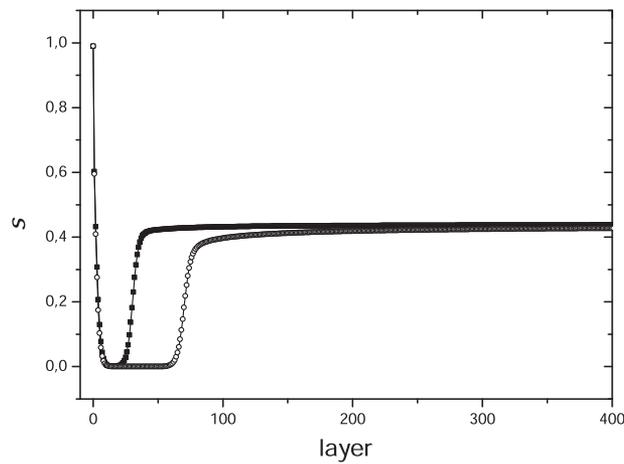

FIG. 7. CS case. Order parameter profile for disordered surface ($\theta_1 = 2.30$) and ordered bulk ($\theta_\infty = 2.18$) for different rates of the interparticle interaction. Filled squares refer to $\epsilon_\ell \sim \ell$ and open circles to $\epsilon_\ell \sim \ell^{0.7}$. The underlying lines are just guides to the eye. $s(0) = 0.99$ and $a_1 = 0$.
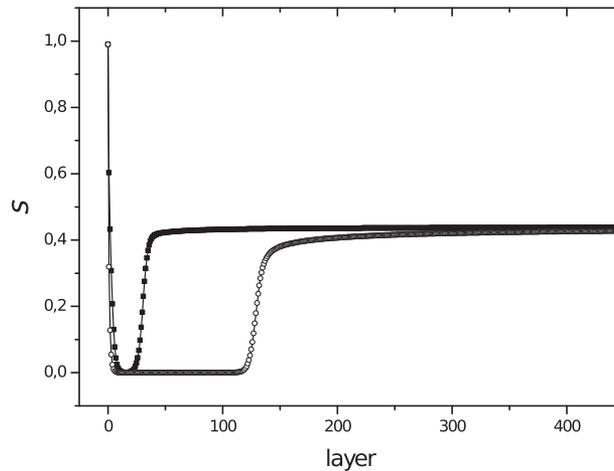
FIG. 8. CS case. Order parameter profile for ordered bulk ($\theta_\infty = 2.18$) and disordered surface. Filled squares refer to $\theta_1 = 2.3$ and open circles to $\theta_1 = 3.0$ on the surface. The underlying lines are just guides to the eye. $s(0) = 0.99$ and $a_1 = 0$.

A step on the profile also appears in the case of a strong mismatch between configurations next to the surface and in the bulk. Fig. 8 illustrates the dependence of the step width on the temperature difference. The bulk is ordered with $\theta_\infty = 2.18$ and we consider two disordered states next to the surface: corresponding to $\theta_1 = 2.3$ and $\theta_1 = 3.0$. We notice that the step width in the latter is wider than in the former case.

In this CS case, as opposed to the PS case, the external potential on the first layer has a small but noticeable effect on the order parameter profile. Fig. 9 corresponds to a situation of an ordered bulk and a disordered surface with a non vanishing external potential on the first layer. Next to the surface the system adjusts itself to meet both anchoring and external potential constraints, then we observe a step associated to a disordered configuration: a negative external potential induces ordering and a narrower step with respect to a positive external potential.

At the end of last subsection (PS case) we showed that the anchoring condition and the external potential have similar effects on that profile. Here, for the CS case, the situation is somewhat different. Suppose the reduced temperature near the surface is high enough to produce a disordered configuration and the reduced temperature in the bulk produces order there. In this case, the anchoring $s(0)$ has no effect on the profile, while the external potential μ_1 can tune the step width.
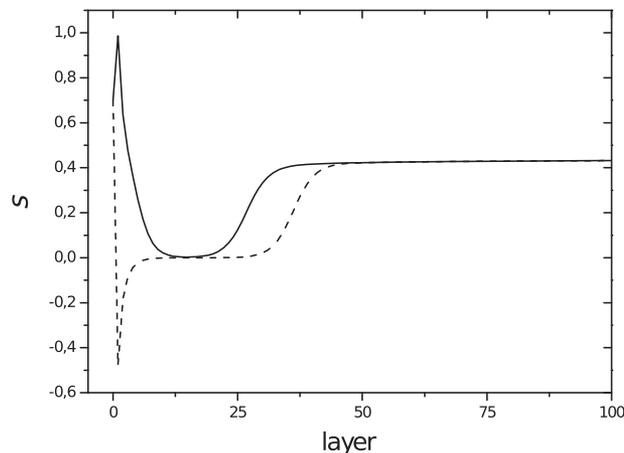

FIG. 9. CS case. Dependence of the profile on the external potential for ordered bulk ($\theta_\infty = 2.18$) and disordered surface ($\theta_1 = 2.3$). Continuous curve: $a_1 = -5.0$; dashed curve: $a_1 = +5.0$. $s(0) = 0.99$.

IV. DISCUSSION

In our lattice model we assume that interactions between rods in different planes (or disks) can be disregarded. In a mean-field approach, this amounts to considering a smaller number of first neighbors. The main consequence of this approximation is a common reduction in all s_ℓ's, besides that, it produces a small decrease in the steps widths, which do not alter the qualitative behavior of the profile.

A first order transition is observed both in the PS and CS cases as expected. All results are robust with respect to the anchoring condition: it does not affect the profiles, except for the rows in the immediate neighborhood of the surfaces. The profiles are primarily determined by the reduced temperature and by the bulk configuration. This behavior is not observed in simulations of similar systems,[11] where profiles are strongly dependent on the anchoring condition. The reason for this discrepancy is that the mean field approach intrinsically favors a preferential direction.

In the PS case, the free energy presents a peculiar behavior. In the first order transition range, we study the subsystem free energy: considering just the first rows next to the wall, the ordered solution is the only stable solution throughout the coexistence region and this feature disappears as we consider larger subsystems. The reason is that we probe a region were the order parameters have not yet reached the equilibrium values corresponding to the imposed temperature. Probably this effect is not particular to this system and it can be found in other systems bounded by a surface. Yet in this case, the external potential on the first row has almost no effect on the profile, just perturbing the rows next to the surface; here, anchoring condition and external potential produce qualitatively the same effect.

In the CS case, the effect of increasing interactions towards the bulk produces very interesting effects. For an ordered bulk and a disordered surface, the profile does not raise monotonically but it presents a step locking into a disordered region before reaching the ordered configuration. The width of this step depends on the slope of the interaction profile, being wider for smoother profiles; the mismatch between the values of the interactions in the bulk and on the surface has also an effect on the width of the steps, larger mismatches produces wider steps. Previous numerical studies on spherocylinders near flat walls have also shown similar steps with increasing concentration.[9] Finally, in this case, as opposed to what happens in the PS case, the external potential does have an influence on the width of this disordered domain: for an ordered bulk and a disordered surface, the chemical potential may assist or retard the approach to the bulk configuration, depending on its sign; this can be observed in terms of the width of the step. In this case, the impact of the anchoring condition and the of external potential are not equivalent. Prediction of the step, its position and width, may be relevant to applications in nanotechnology.

V. CONCLUSION

Motivated by recent experiments on colloidal particles with dimensions comparable to the confining volumes, we propose a model to describe the orientation of rods in the presence of planar and curved surfaces; in the latter, the dimensions of the cylinders with respect to the curvature radius imply in excluded volume interactions that drive the system into an ordered domain. We propose a lattice model to describe such systems and map it onto a three-state Potts model[14] which is solved within a mean-field approach.[16] In the curved case, the effect of the curvature is obtained by row dependent interparticle interactions. For both types of surfaces, we obtained the free energy and the orientational profile, which were studied under various conditions.

Our model brings about two main results. The first concerns the planar surface case: it predicts a peculiar behavior of the free energy. The second is related to the curved surface case: in situations where the system orders towards the bulk, the order parameter profile does not raise monotonically, but it presents a step associated to a disordered domain.

A shortcoming of our study is the weak influence of the anchoring on the overall profile. The constraint of fixed number of rods in every row must also be released. An extension of the present work is under progress, which allows for vacancies. This will enable us to have a varying concentration and

make further comparison with simulations and experimental results.[9,11,12] Finally, another possibility is to investigate the decrease in the alignment of rods in the vicinity of the outer part of a sphere, which could described by a sequence of decreasing interactions.

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