

# Isotropic-Nematic transition of long thin hard spherocylinders confined in a quasi-two-dimensional planar geometry.

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We present computer simulations of long thin hard spherocylinders in a narrow planar slit. We observe a transition from the isotropic to a nematic phase with quasi-long-range orientational order upon increasing the density. This phase transition is intrinsically two dimensional and of the Kosterlitz-Thouless type. The effective two-dimensional density at which this transition occurs increases with plate separation. We qualitatively compare some of our results with experiments where microtubules are confined in a thin slit, which gave the original inspiration for this work.

## I. INTRODUCTION

Two-dimensional systems behave generically in a qualitatively distinct way from three-dimensional ones. In experiments, they are often not strictly confined to a mathematical surface, but also span a small region in the transverse dimension. A situation where two hard walls very close to each other confine the system occurs between the two extremes of bulk and two-dimensions, and, for this reason, is interesting to analyze. We study the phase behavior of a system confined between two parallel planar plates separated by small distances as a function of the plate separation and relate it to the corresponding strictly two-dimensional system. We address this question, using computer simulations, for the Isotropic-Nematic (I-N) transition of thin, hard spherocylinders. The inspiration for this problem comes from a biological system, cortical microtubules in plant cells, and by in vitro experiments on microtubules confined in thin samples. Microtubules are tubular polymers of the protein tubulin with an aspect ratio of a few hundreds. They are the stiffest polymers available to eukaryotic cells, with a persistence length of about 3 millimeters [1], two orders of magnitude greater than their typical length. With microtubules one can construct a good model system for the quasi-two-dimensional regime of (broadly polydisperse) hard rods. In this paper, we focus on the results of our simulations, while also commenting on the possible links to the experimental system.

It is known [2, 3] that a system of hard needles or high ( $> 9$ ) aspect ratio disco-rectangles in two dimensions exhibits, similarly to the xy-model, a nematic transition to quasi-long-range order of the Kosterlitz-Thouless kind [4]. The role of disclinations in this system has been investigated for different two-dimensional geometries [5]. A related problem is that of surface effects in presence of a single wall [6, 7, 8]. Several theoretical and simulation studies were focussed on fluids of hard rods in contact with hard walls. Chen and Cui performed density functional theory calculations for a fluid of hard semiflexible polymers near a hard wall. They show a weakly first-order uniaxial to biaxial transition (signature of two dimensional ordering in the plane defined by the wall) at a bulk density far below that of the bulk I-N transition [9]. They also observe that the formation of a biaxial nematic film at the wall-isotropic fluid interface with the director parallel to the wall. The thickness of this film appears to diverge as bulk I-N coexistence is approached [9]. A surface induced continuous transition from a uniaxial to a biaxial phase prior to complete wetting was also predicted by density-functional theory of the Zwanzig model [8, 10], in which the orientations of the particles are restricted to three orthogonal directions, and confirmed by simulations for freely rotating spherocylinders [8, 11]. Returning to the case of a fluid confined by two parallel hard walls, it was found by simulations of freely rotating spherocylinders [11] and by density functional theory calculations of the Zwanzig model [10] that the surface-induced uniaxial to biaxial transition is prior to a first-order capillary nematization transition at larger bulk densities, which terminates in a capillary critical point when the wall separation is about twice the length of the rods.

This paper is organized as follows. In section II we present our model of hard spherocylinders confined between two parallel planar hard walls, and we introduce the quantities that are measured, namely, the nematic order parameter

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and the orientational correlation function. In section III, we present the results and we discuss the polydisperse case and the possible connections with the experimental system. Our main result is that similarly to the strictly two-dimensional system, there is no true transition to long range order in the thermodynamic limit. A thickness-dependent transition to quasi-long range orientational order of the Kosterlitz and Thouless kind is present instead.

This is in qualitative agreement with what is observed experimentally in a system of microtubules.

## II. A FLUID OF HARD SPHEROCYLINDERS CONFINED IN A QUASI-TWO-DIMENSIONAL PLANAR SLIT

We perform Monte-Carlo simulations for a fluid of hard spherocylinders with a (mean) length-to-diameter ratio  $L/D = 320$ , corresponding to microtubules of  $8 \mu m$  in length and  $25 nm$  in diameter, confined between two planar hard walls with an area of  $L_x \times L_y$  in the  $x - y$  plane at distance  $h = H/D$  in the  $z$  direction (see Fig. 1). Periodic boundary conditions are employed in the  $x$ - and  $y$ -direction. The slit width  $h$  varies from 1 to 120. We perform simulations both of a system of monodisperse rods and a system of polydisperse rods with an exponential length distribution, which resembles closely the experiment with microtubules (see Section III). The simulations consist of about  $2 \cdot 10^6$  Monte Carlo sweeps, where one sweep equals one attempted move per particle. Typically more than  $10^5$  Monte Carlo sweeps were allowed for equilibration. The number of particles  $N$  in a simulation is up to 5000, although typically lower than 2000.

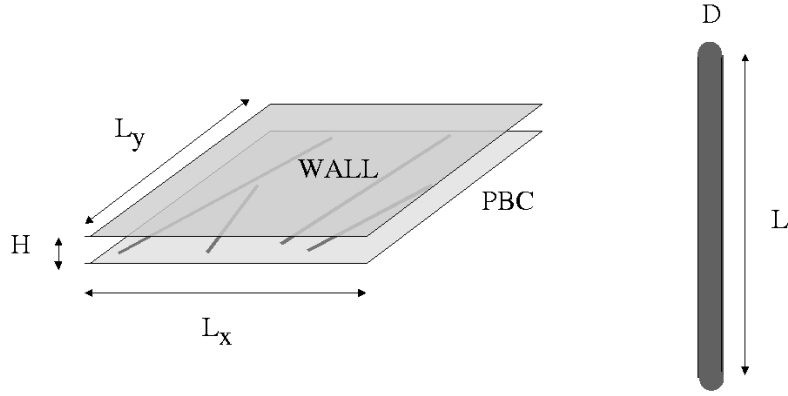


FIG. 1: A schematic picture of the system, which consists of a slit of thickness  $h = H/D$ , enclosed by two planar hard walls in the  $x-y$  plane with dimensions  $L_x \times L_y$ . A particle (spherocylinder) is described by a cylinder of length  $L$  and diameter  $D$  capped by two hemispheres of the same diameter. Periodic boundary conditions are applied laterally.

We perform simulations for monodisperse spherocylinders for varying dimensionless densities:

$$C = \frac{N}{V}(L + D)^2 D,$$

where  $N$  is the number of particles,  $V = L_x L_y H$  is the total volume. We measure the eigenvalues of the standard  $3 \times 3$  nematic order-parameter tensor

$$Q_{\alpha\beta} = \left\langle \frac{1}{N} \sum_{i=1}^N \left( \frac{3}{2} u_{\alpha}^i u_{\beta}^i - \frac{\delta_{\alpha\beta}}{2} \right) \right\rangle,$$

where  $\alpha, \beta = x, y, z$ ;  $u_{\alpha}^i$  is the  $\alpha$  component of the unit vector defining the orientation of particle  $i$ , and  $\delta_{\alpha\beta}$  is Kronecker's delta. Diagonalizing  $Q_{\alpha\beta}$  gives the orientational order parameters. As the typical cylindrical symmetry

of the nematic state is broken a priori by the geometric constraints on the system, the most suitable order parameter  $\Delta$  is proportional to the difference between the two highest eigenvalues of the average nematic tensor, normalized with a factor of  $2/3$  to make it lie in the interval  $[0, 1]$ . It is easy to realize that when  $h = 1$  this quantity reduces to the two-dimensional nematic order parameter [2] and for larger  $h$  it can be identified with the biaxial order parameter [8]. In fact, for  $h = 1$ , one of the three eigenvalues of  $Q$  will be  $-1/2$  due to the geometric confinement, so that the submatrix defined by the other two eigenvalues will coincide with the exception of a constant factor with the two-dimensional nematic order parameter  $2 \times 2$  tensor, and

$$\Delta \sim S = \left\langle \frac{1}{N} \sum_{i=1}^N \cos(2\theta_i) \right\rangle,$$

where  $\theta_i$  is the planar smallest angle formed by the  $i$ -th particle with the nematic director, and  $S$  is the 2-dimensional orientational order parameter. We also examine the density and orientational order parameter  $\Delta$  profiles along the axis orthogonal to the walls. These are measured using bins with a typical width of about  $D$ , accumulated over the sweeps in the simulation [8]. Lastly, we measure the orientational correlation function

$$g_2(r) = \langle (\cos(\theta(0) - \theta(r))) \rangle,$$

which describes the decay of the long wavelength fluctuations in the orientation.

### III. RESULTS

We will first discuss the monodisperse case. The polydisperse system will be examined briefly, motivated by its relevance to experiments with microtubules.

#### Order parameter and size effects.

Fixing the lateral size  $L_x = L_y = L_{xy}$  of the system, we measure the order parameter  $\Delta$  as a function of  $C$ . We find a transition to an ordered state for a density which depends slightly on  $h$ . In figure 2 we show typical snapshots of the fluid of spherocylinders for different densities of rods and a lateral view of the simulation box to illustrate its thickness. A transition from a uniaxial phase (in which the rods are randomly oriented in the  $xy$  plane) to a biaxial phase (the rods have a preferred orientation in the  $xy$  plane) is apparent from visual analysis of these pictures. The order parameter and its profile along the  $z$ -axis as a function of density are plotted for a few examples in figure 3. We define arbitrarily the apparent transition density  $C_{\text{trans}}$  as the density at the intersection of the tangents constructed on the low density part and the linearly increasing part of  $\Delta(C)$  at fixed density (see the caption of figure 3).

The apparent phase transition from a uniaxial to biaxial phase, however, depends in all instances on the lateral size of the system. In fact, the order parameter drops with increasing size at fixed  $C$ , in a way that the apparent transition density increases. We measured this effect consistently for different transverse sizes ( $h = 5, 20, 40, 60$ ). In figure 4 we report an example for  $h = 20$ .

This fact gives a hint that, as in the strictly two-dimensional system, there could be no true phase transition in the thermodynamic limit, but a transition to quasi-long-range order. To establish this, it is necessary to test whether the orientational correlation function shows an algebraic decay (see below).

For comparison with real finite size systems it is interesting to look at the apparent transition density  $C_{\text{trans}}$ , at fixed lateral size  $L_{xy}$ , varying the small transverse size  $h$ . Two examples of the resulting phase diagrams are reported in figure 5. The transition density is roughly constant for thicknesses lower than  $h = 15$  (see Fig. 5b) and increases almost linearly for thicker boxes (see Fig. 5a).

#### Correlation function

As we argued in the previous section, because of the finite size effects (decrease of  $\Delta$  with increasing size), little can be concluded about the nature of the phase transition, or even its existence based on the measurements of the order parameter. These finite size effects, together with the presence of a phase transition to quasi-long-range order in the strictly two-dimensional system, make it sensible to investigate the decay of long wavelength orientational fluctuations. This is a delicate matter due to the very long relaxation times of these soft modes. We investigated the transition for integer values of  $h$  up to  $h = 10$ , with a simulation box having a lateral size  $L_{xy} = 4000D$ . Above

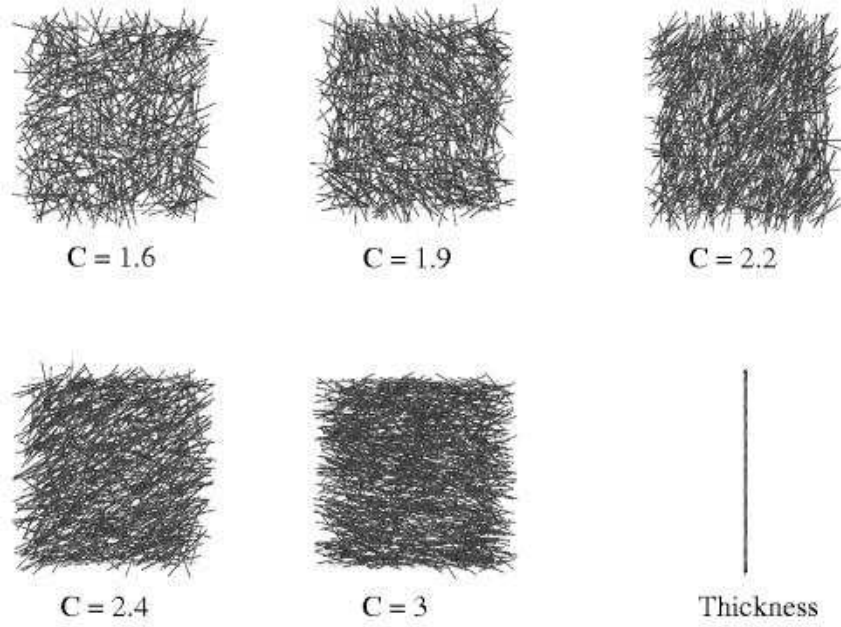


FIG. 2: Snapshots of the configuration of the system projected on the  $xy$  plane for different values of the dimensionless density  $C = N/V(L + D)^2D$ . Here  $h = 20$ ,  $L_{xy} = 1400D$ ,  $N$  varies from 600 to 1150 and the equilibration time is  $10^6$  sweeps. The diameters of the rods are not drawn to scale.

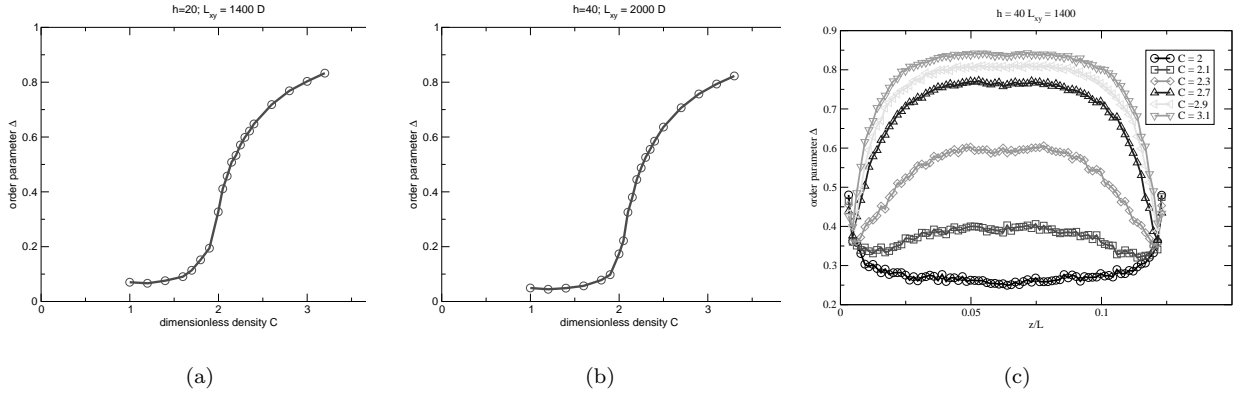


FIG. 3: (a) and (b). Order parameter  $\Delta$  as a function of non-dimensional density for  $L_{xy} = 1400D$ . (a)  $h = 20$  (b)  $h = 40$ . (c)  $z$  profile of the order parameter for  $h = 40$ ,  $L_{xy} = 1400D$  and increasing density. The transition density  $C_{\text{trans}}$  can be defined through the intersection of the tangents constructed on the low density part and the linearly increasing part of graphs like (a) and (b).

this thickness, the number of particles was too high to achieve relaxation in reasonable times. In all these cases  $g_2(r)$  showed a transition from exponential to power law decay with increasing density. One example, for  $h = 6$ , is plotted in figure 6. This transition does not depend on the size of the system, which just needs to be large enough so that the correlation of the modes is not affected by the periodic lateral boundary conditions.

From the above data, we can conclude that we are observing the same phase transition as in the two dimensional system of needles, described by the Frank elastic free energy,

$$F = \frac{1}{2}K \int \nabla \theta(\mathbf{r}) d\mathbf{r}.$$

Therefore we can set the transition density  $C_{\text{trans}}^{KS}$  when the exponent of  $g_2$  crosses  $1/4$  [2]. Going to the limiting case  $h = 1$ , we can recover the fully two-dimensional system and compare the transition density with the one given

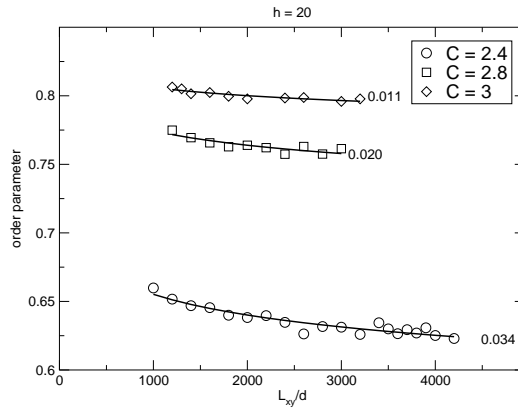


FIG. 4: Finite size effects in the measurement of the order parameter  $\Delta$ . The graph shows the decay of  $\Delta$  for three dimensionless densities as a function of the lateral size  $L_{xy}$  when the vertical size  $h = 20$  is kept fixed. The numbers to the right of the curves are the exponent from power law fits. The decay of the order parameter for increasing size causes a shift in the apparent transition.

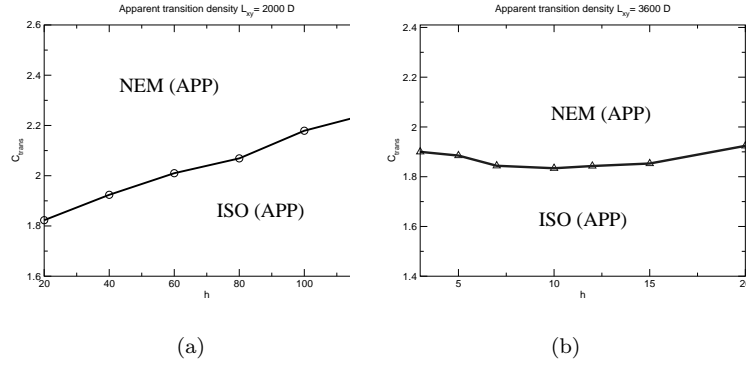


FIG. 5: Phase diagrams for the apparent nematic transition at fixed lateral size  $L_{xy}$ . The reduced uniaxial-biaxial transition density  $C_{\text{trans}}$  for different values of  $h$ . (a) Lateral size  $L_{xy} = 2000D$ , thickness from  $h = 20$  up to  $h = 120$ ; the number of particles  $N$  for these runs is up to 7000. (b) Lateral size  $L_{xy} = 3600D$ , thickness up to  $h = 20$ ,  $N$  up to 6000. The two critical lines in (a) and (b) do not connect continuously at  $h = 20$  because of the finite size effects

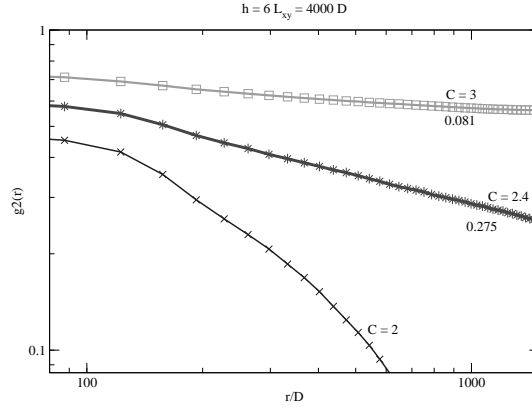


FIG. 6: Log-log plot of the orientational correlation function  $g_2(r)$  for different values of the density, in the case  $h = 6$ . For low density this quantity has exponential decay, which becomes algebraic with increasing  $C$ . The numbers next to the curves indicate the decay exponents from power-law fits. By convention, the transition is defined to be where the exponent of the correlation function crosses  $1/4$ , in this instance around  $C = 2.4$ .

in [2]. We measure a  $C_{\text{trans}}^{KS}(h=1) = 6.5$  which we consider in good agreement with the 7.5 to 8 of Frenkel and Eppenga, considering the longer relaxation times we allow ( $5 \cdot 10^5$  sweeps for up to 2600 particles). This value can also be compared with the 5.3 found in [3] for disco-rectangles with  $L/D = 15$ . The most interesting question, though, is how the transition density changes as a small lateral dimension is added. By a naive argument comparing the three-dimensional density  $C$  with the two dimensional one  $C_{2d} = \frac{N}{L_x L_y} (L + D)^2$  one would expect to see a transition density which goes like  $1/h$  so that the “effective” two-dimensional density is kept fixed. However, according to our data, shown in figure 7, this decay is slower than this power law. We can try to understand this by a qualitative argument based on the fact that this two dimensional transition is mediated by defects. Adding a small transverse dimension, the liberty of effective overlaps given by the third degree of freedom makes it harder to form a disclination, so that a higher density than just  $h$  times the two-dimensional one is required to achieve the transition. This fact is illustrated in figure 8, where we show two typical xv-projections of the nematic states for  $h = 1$  and  $h = 3$ . The configurations are qualitatively

are noticeable.

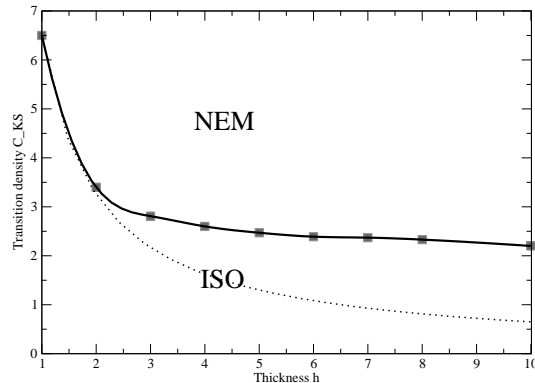


FIG. 7: Phase diagram for the nematic transition in quasi two dimensional geometry. The Kosterlitz-Thouless transition density  $C_{\text{trans}}^{KS}$  is plotted as a function of the system thickness  $h$ . Its decay is slower than the naively expected  $1/h$  indicated by the dotted line.

### Broadly polydisperse rods

We performed similar simulations for a system of polydisperse rods with an exponential length distribution. Our main motivation for doing this was to predict the experimental behavior of microtubules when they are confined in a region with a thickness that is very small compared to their (mean) length and very large compared to their diameter. The sample for this experiment consists of a microscope coverslip patterned with  $1\mu\text{m}$  thick photoresist used to maintain a constant separation with the microscope slide (details will be published elsewhere) [12]. In the experiment microtubules are broadly polydisperse, and typically show an exponential distribution in length with an average aspect ratio of a few hundreds.

In the polydisperse case, the apparent transition at fixed size is broader than the one observed for the monodisperse system (figure 9) and its onset is at lower densities, due to the effect of long rods. Nevertheless, the qualitative behavior of the system is the same, with size effects and power-law decay in the correlation function. By measuring the total length of the rods in one box, knowing that the length of a tubulin dimer is 8 nm and that each polymer is composed of 13 protofilaments, one can predict the concentration of tubulin needed to have the ordering transition at a fixed size. The size of the system can be set as the field of view of the microscope, which is effectively the scale at which the experimental system is observed. With this identification, the apparent transition density, expressed in terms of tubulin concentration, falls in the experimentally accessible region of 2 to 5 mg/ml of tubulin.

These results are qualitatively consistent with those observed experimentally (see figure 10 as an illustration). Also, in the experiment, microtubules are observed to order in “patches” of tens of microns in size, which is consistent with the absence of true long range order predicted by the simulation. Quantitative work on the experimental system is still in progress [12].

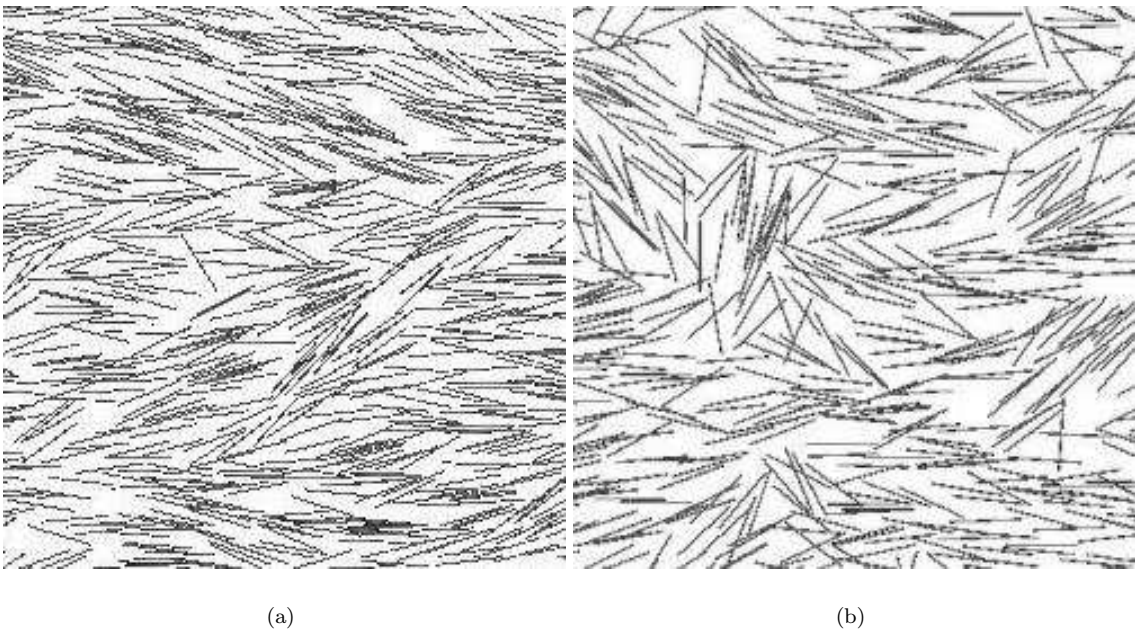


FIG. 8: Typical snapshots of configurations of two dimensional nematic-like phases (details). The pictures are projections of the configurations on the  $xy$ -plane. (a) 3074 particles in a slit with  $h = 1$ ,  $L_{xy} = 6000D$ . The defects are noticeable in the picture. (b) 1150 particles in a slit with  $h = 3$ ,  $L_{xy} = 4000D$ . Along with the defects, overlaps between projections of particles due to the transverse degrees of freedom are visible.

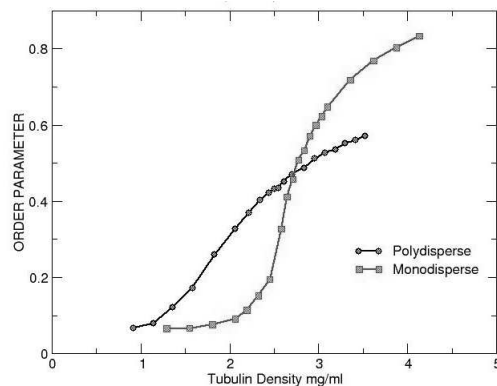


FIG. 9: Apparent transition predicted by the simulation in the exponentially polydisperse case for a fixed size  $L_{xy} = 1200D$  ( $30 \mu m$ ) compared to the monodisperse system with the same mean aspect ratio (320). This size is comparable with that of a field of view of the microscope. In the x-axis we plot the tubulin density estimated from the total length of the rods in the simulation box.

#### IV. CONCLUSIONS AND PERSPECTIVES

We presented a Monte Carlo simulation of hard spherocylinders confined between two parallel walls at a small distance. This computation was intended to test the behavior of the nematic transition in a quasi-two-dimensional system. The main result is that a transition to long-range-order is absent in the thermodynamic limit which is substituted by a Kosterlitz-Thouless-like transition revealed by the algebraic decay of the orientational correlation function. This is in qualitative agreement with what is observed experimentally for a broadly polydisperse system of rod-like biological polymers (microtubules) and has some interesting general consequences. First of all, it indicates that a system with some small transverse third dimension will maintain the same qualitative behavior as a true two-dimensional one. Secondly, the slower decrease of the Kosterlitz-Thouless transition with increasing plate separations

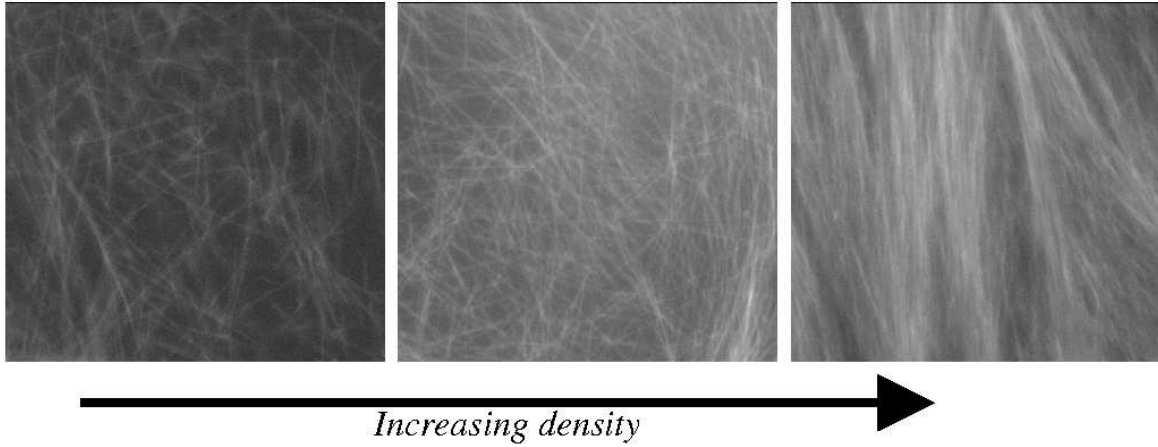


FIG. 10: Snapshots from the experiment. The microtubules, confined in  $1\ \mu\text{m}$  thick microscope slides, are imaged with fluorescence microscopy. The concentration range of polymerized protein is 2-4 mg/ml. The rods are observed to align for increasing densities on scales comparable to the field of view of the microscope (30-100  $\mu\text{m}$ ). On larger scales, patches of aligned rods with different orientation are noticeable.

for the 2D-like isotropic-nematic transition indicates that there is an important role played by the transverse degree of freedom in the elimination of disclinations. Possible future work includes a quantitative exploration of the experimental system. It is also interesting to investigate in more detail the crossover between two- and three-dimensional behavior, exploring slit thicknesses that are comparable with the length of the rods. This kind of work would require using spherocylinders with a lower aspect ratio, to keep the number of particles, and therefore the computational cost, reasonably low. One possibility that we can hypothesize is that the Kosterlitz-Thouless transition in the strictly two-dimensional and quasi-two-dimensional system ends in the previously observed wall-induced uniaxial to biaxial transition [8] at larger plate separation and is therefore not connected to capillary nematization (a transition from a biaxial to a condensed nematic phase), which terminates in a critical point at a fixed plate separations [10].

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