

Phase behavior of wormlike rods

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(Received 7 November 2007; published 27 May 2008)

By employing molecular dynamics computer simulations, the phase behavior of systems of rodlike particles with varying degree of internal flexibility has been traced from the perfectly rigid rod limit till very flexible particles, and from the high density region till the isotropic phase. From the perfectly rigid rod limit and enhancing the internal flexibility, the range of the smectic-A phase is squeezed out by the concomitant action of the scarcely affected crystalline phase at higher density and the nematic phase at lower density, until it disappears. These results confirm the supposition, drawn from previous theoretical, simulational and experimental studies, that the smectic-A phase is destabilized by introducing and enhancing the degree of particle internal flexibility. However, no significant changes in the order of nematic-to-smectic-A phase transition, which appears always first order, nor in the value of the layer spacing, are observed upon varying the degree of particle internal flexibility. Moreover, no evidence of a columnar phase, which was thought of as a possible superseder of the smectic-A phase in flexible rods, has been obtained.

DOI: 10.1103/PhysRevE.77.051705

PACS number(s): 61.30.St, 64.70.M-, 66.30.Xj

Particles with only steric, repulsive interactions are basic models with which to study the phase behavior and properties of condensed matter systems. If the particles are anisometric, a rich phase behavior may be observed, with the crystalline and isotropic fluid phases possibly bracketing phases of intermediate order. Hard spherocylinders [1] provide an emblematic example. They were shown to exhibit first smectic-A (S_A), and then also nematic (N), liquid-crystal phases upon increasing the aspect ratio [2]. Hard spherocylinders and related models are pertinent to a host of experimental systems where lyotropic liquid crystals take place. They include systems of biological, organic and inorganic origin. Examples are TMV and *fd* viruses [3], DNA [4], β -FeOOH particles [5] and rod-shaped Carbon nanotube [6] and nanocrystals [7]. For many of these systems, however, rigid models provide only a first good approximation. In fact, most of the particles constituting the experimental suspensions are, to a certain extent, flexible. Internal flexibility is expected to influence the self-assembly characteristics of the rodlike particles. The comprehension of self-assembly mechanisms is important per se but also because, as in the case of nanorods, their strict relationship with the properties of the sample may contribute to a successful exploitation of the materials. Here, the study of a completely rigid rodlike model, performed earlier [8], has been extended to investigate the effect of internal flexibility on the phase behavior of rodlike systems.

To this end, systems of elongated particles have been simulated with the molecular dynamics (MD) technique [9]. The particles, of mass m , are wormlike and formed by nine beads. Within a particle, contiguous beads are kept at a fixed distance of 0.6σ , σ being the quantity defining the scale of lengths, while a harmonic bending interaction exists between three contiguous beads, l and n , m :

$$v_{lmn}(\theta) = \frac{1}{2}K(\theta - \pi)^2. \quad (1)$$

In the equation above, v_{lmn} is the angular potential energy, θ is the angle formed by the two relevant bonds, and K the force constant regulating the degree of internal flexibility. In addition, between two noncontiguous beads a repulsive interaction exists of the following form:

$$u_{ij}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right], & r \leq 2^{1/6}\sigma, \\ 0, & r > 2^{1/6}\sigma. \end{cases} \quad (2)$$

In the equation above, u_{ij} is the interaction potential energy between beads i and j , separated by a distance r , while ϵ is the quantity defining the scale of energies. Equation (2) describes also the interaction potential energy between any two beads belonging to two different particles, so that the interaction potential energy between the wormlike rods I and J is given by

$$U_{IJ} = \sum_{k=1}^9 \sum_{j=1}^9 u_{k,j}. \quad (3)$$

Systems of $N=600$ wormlike particles have been simulated for several values of K , covering six order of magnitude of the force constant, ranging from perfectly rigid to very flexible rods. The computations have been performed at a fixed pressure of $P^* = 24.716 \frac{\sigma^3}{\epsilon}$ and varying the temperature $T^* = k_B T / \epsilon$, with k_B the Boltzmann constant. Pressure and temperature have been maintained at the preselected values with either the Nosé-Hoover thermostat, coupled with the Parrinello-Rahman barostat or the weak coupling method [9]. Every set of simulations has been started at a low enough T^* with a highly ordered configuration where all rods were completely stretched along the z axis of the laboratory frame of reference and arranged in a hexagonal closed packed fashion. Simulations at higher values of T^* have been started from an equilibrated configuration at a lower tem-

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perature. For every value of K , at least 10 values of temperature have been examined, but for the more rigid cases this number has been doubled.

Generally, equilibration run of 10^7 time steps have been performed, followed by as many time steps of production. The time step employed has been $1.36 \times 10^{-4} t^*$, with $t^* = (m/\epsilon)^{1/2} \sigma$.

Additional simulation runs have been performed for certain values of K and T^* on larger systems of 2400 particles. Transition temperatures have been observed to remain within 5% of those determined, as described next, for the smaller systems.

Via the calculations of the hexatic (Ψ_6), smectic (τ), nematic (S_2) order parameters (for the definition of these order parameters see, e.g., Ref. [8]), four phases have been identified. The crystal (or smectic-) B phase, where all order parameters are positive; the smectic- A phase, characterized by Ψ_6 equal to, and the other two order parameters larger than, zero; the nematic phase, with only S_2 being nonzero; and the isotropic phase where all parameters do, or essentially, vanish. The resulting phase behavior is depicted in Fig. 1, where the sequence of phases is shown either as a function of T^* and of ϕ , the packing fraction [10].

Lots of work have been done on the isotropic-to-nematic phase transition [11–13]. The consensus reached is general. Flexibility increases the density at which this phase transition occurs. The results of Fig. 1 clearly agree with this picture. In common to prior simulations on short hard spherocylinders [2], only a single coexistence density is reported in this figure, as the I - N phase transition in all range of internal flexibility is so weak that the two relevant coexistence densities cannot be clearly discerned.

Significant less attention has been dedicated so far to the smectic phases in systems of semiflexible rods. The higher density part of the phase diagram of Fig. 1 is therefore of primary concern in the present work. Around 10 years ago a set of theoretical, simulational, and experimental papers appeared on the N - S_A phase transition in semiflexible rod systems [14–17], while more recent theoretical results on this subject have been reported in Refs. [18,19].

Experiments on suspensions of the long and slightly flexible fd virus revealed that the N - S_A phase transition in these systems is of first-order character and occurring to a packing fraction of ~ 0.75 , while the layer spacing of the inhomogeneous phase was very close to the rodlike particle length. By comparing these results with either numerical data on systems of perfectly aligned hard rods and the analogous phase transition in the suspension of TMV virus, it was speculatively concluded that flexibility has three basic effects on the N - S_A phase transition: (I) it shifts the N - S_A coexistence densities to higher values; (II) it drives the transition to being first order; (III) it reduces the layer spacing.

Concomitantly, two theories, one phenomenological in character [15], the other [16] based on an extension of the Khoklov-Semenov theory [11] to the N - S_A phase transition, were developed, both adding support to the conjectures coming from the experimental work. The most recent theory of Ref. [18] is also confirming these conjectures.

The work of Ref. [15] illustrates the basic mechanism responsible for the effect of flexibility on the N - S_A phase

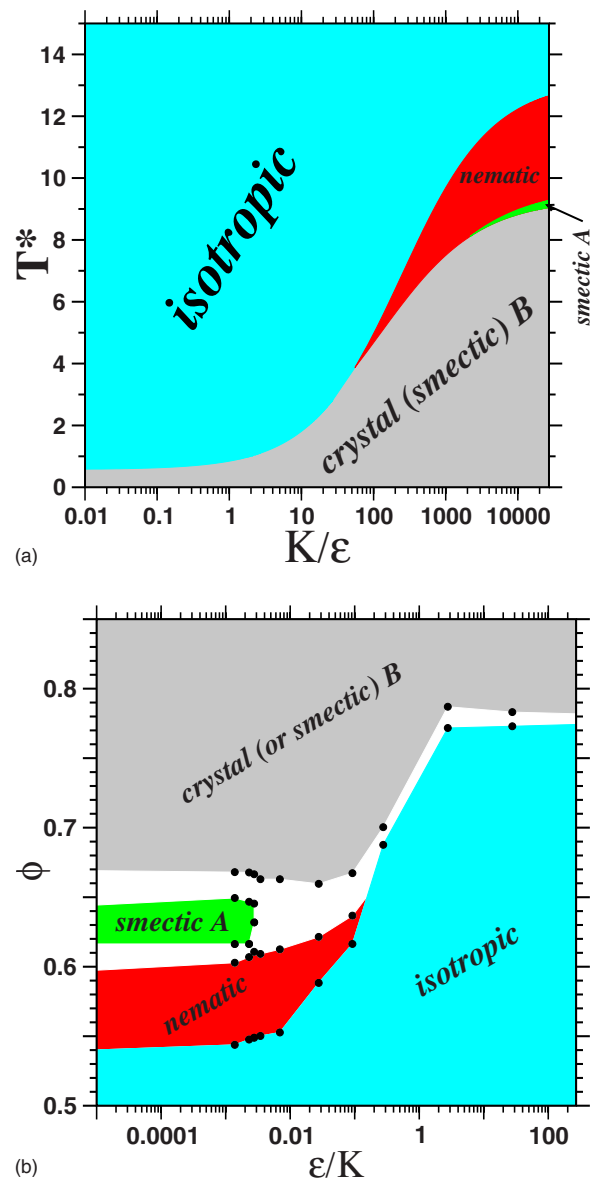


FIG. 1. (Color online) Phase diagram of the semiflexible nine beadlace model as a function of internal flexibility degree. In the top panel the K/ϵ versus T^* plane is shown, while in the bottom panel the ϵ/K versus ϕ plane is reported. In both panels, the regions of existence of the various phases are indicated by the respective labels, while the white region in the bottom panel is the coexistence region. In panel (a), the transition temperature curves are obtained by fitting the corresponding computer simulation data with power law functions of the type $a \frac{b+K^\alpha}{c+K^\alpha}$. In panel (b), the coexistence data obtained in the computer simulations are reported as black dots, and the lines connecting them are just guides to the eye.

transition in perfectly aligned rods, originally put forward in Ref. [20]. The formation of a smectic- A phase is entropically driven by the collective tendency of the rods to fill the voids present at each end of the particles in the nematic phase. Although forming layers has a free energy cost, in that way the rods fill those voids and gain much free volume in the directions perpendicular to the layer normal, thus reaching a state of overall larger entropy. By letting the particles deflect, the abovementioned voids can be more efficiently filled al-

ready in the nematic phase by an appropriate bent of the chain. The net result is that the nematic-smectic phase transition is postponed to a higher density.

The results of the present work are certainly not in contrast with this picture. Indeed, the density at which the nematic phase remains stable increases with increasing flexibility. In both the oldest theoretical works [15,16], only spinodal calculations were performed so nothing could be said about the actual density gap characterizing the phase transition, and thus no conclusion could be given about the order of the latter. Binodal points have been instead evaluated in the work of Ref. [18], where it is found that the $N-S_A$ transition is quasisecond order in the perfectly rigid rod case and that flexibility drives the character of this transition to be first order. In this work, in agreement with previous results on the completely rigid version of the present model [8], as well as on hard spherocylinder systems [2,21], it is observed that the $N-S_A$ transition is actually always first order, being characterized by a finite density gap and a discontinuity of the smectic order parameter τ . The density gap seems to slightly decrease by introducing and increasing the internal flexibility. In fact, while the nematic coexistence line increases with increasing particle flexibility, that of the smectic-A phase remains essentially constant, at least in the regime where the rods can be considered only slightly flexible. This fact appears in agreement with a more recent observation on the effect of flexibility on the $N-S_A$ phase transition in M13 virus suspensions [22]. In these experiments the lowest packing fraction at which the smectic-A phase is observed was found to be strongly dependent on the value of ionic strength, in contrast with the previous results for the *fd* virus suspensions, but essentially independent on the degree of particle flexibility. For the largest value of ionic strength considered, for which the rodlike virus particles may be more closely assimilated to rods interacting through repulsive and short-range interactions, the abovementioned characteristic packing fraction can be estimated to be around 0.6–0.7, that is in good agreement with what one can observe in Fig. 1.

Thus, the abovementioned conjecture about the effect of flexibility on the order of the phase transition is not supported by the present numerical data. It must be said that this conjecture was originated by a comparison between systems, such as perfectly aligned hard rods on the one hand, and *fd* virus suspensions on the other which cannot be directly linked. In addition, in the present work, no significant changes of the value of the layer spacing has been observed upon introducing and increasing the degree of particle flexibility, nor there have been significant variations of the population of rods which, in the smectic-A phase, lie perpendicular to the director and stay between two layers [23]. The fraction of these rods have been observed to be always tiny and there are no indication, as suggested in Ref. [16], that it increases upon letting the particles be flexible.

The abovementioned mechanism [15] describing the formation of the smectic-A phase in rodlike particle system can be used to justify the observed insensitivity of the density at which the S_A appears for sufficiently stiff rods, and the subsequent increase of this characteristic density for more flexible rods. Smectic-A configurations in which rods are completely stretched along their contour axis and organized in

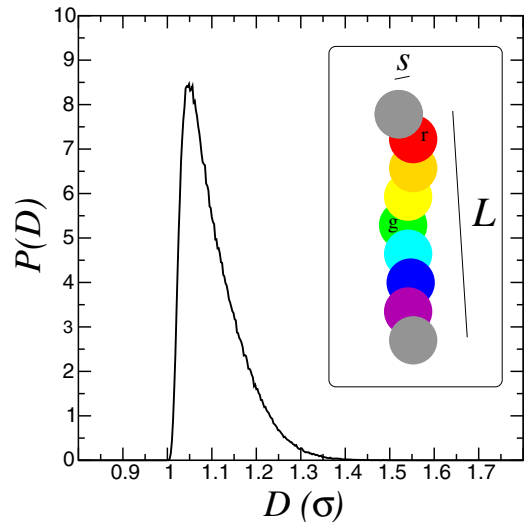


FIG. 2. (Color online) Distribution function of the rod effective diameter. The curve refers to the case of $K=5555\epsilon$ and $T^*=8.85$, where the system is in the S_A phase. The inset is an illustration of the definition of L and s , the two quantities entering the adopted definitions of effective length and diameter of a wormlike rod [24]. Thus, L is the distance between the two extreme (gray) beads, while s , in the particular case shown, is the distance between the centers of the r (red) and g (green) beads, resolved along the line joining the two gray beads.

liquidlike layers of sufficiently high densities correspond to a favorable free energy because the rigid conformation is that of minimum energy and the rods already have found in the smectic structure a favorable way to assembly. It is only when the degree of flexibility is large enough, and the nematic configurations progressively correspond to a more favorable free energy, that the smectic organization become advantageous only at higher and higher density.

The results of Fig. 1 reveal indeed that for sufficiently flexible rods the smectic-A phase disappears being squeezed out by the nematic phase at lower density and a hexatic phase at higher density. These results are the confirmation of the past statement often found in the literature that the smectic-A phase can be ousted by other positionally ordered structures for sufficiently flexible rods.

The present simulations have found that this phase has both a layered structure and a in-layer hexagonal arrangement of the particles, i.e., it is of the crystalline or smectic- B type. In the stiff rod regime, it is worthwhile noticing that there is an indication that the enhancement of internal flexibility favors the B phase with respect to the S_A phase, as the density at which the B phase remains stable is slightly reduced. This can be understood by observing that the principal effect of introducing and increasing flexibility in stiff rods is to increase their effective diameters. For example, for the value of $K=5555\epsilon$ and at a temperature of $T^*=8.85$, the average length of a rod is only 0.2% lower than that corresponding to the fully stretched conformation, whereas the average diameter is 10% larger than that corresponding to the perfectly rigid rod, as one can appreciate in Fig. 2, where the distribution function $P(D)$ of the rod effective diameter D is shown [24]. Thus, the rods are effectively thicker, so

that their projections onto planes perpendicular to the director are quasi-two-dimensional disks of larger diameters. This induces, in those that may be assimilated to a quasi-two-dimensional systems of disks, a crystallization transition at a lower density. Thus, the smectic-*A* phase results to be bracketed by the *B* and nematic phases until a triple-*B*-phase–smectic-*A*–nematic point is reached, after which smectic-*A* phase is no more observed, and a direct *B* phase–nematic phase transition occurs. For smaller values of *K* the density at which the *B* phase remains stable starts to increase. In the same regime the nematic phase interval becomes thinner until a *B* phase–nematic–isotropic triple point emerges after which a direct *B* phase–isotropic phase transition takes place.

The phase diagram of Fig. 1 is qualitatively similar to those resulting from a few theoretical calculations [25,26]. In particular, it is in a certain accord with the phase diagram

presented in Ref. [25], if one identifies their hexagonal phase with the *B* phase described in the present work and forget about the smectic-*A* phase, not taken into account in the theoretical calculations of Ref. [25]. It should be also said that when referring to the hexagonal phase, the authors of Ref. [25] mean a hexagonal columnar phase of the type often exhibited by discotic liquid crystals [27] and also observed in suspensions of DNA [4]. However, columnar order has been never observed in this work. Perhaps, this is because the contour length of the rods is not large enough. Computer simulations on longer rods could help clarifying whether internal flexibility could really favor the formation of columnar phase in long rods or the formation of this mesophase in the abovementioned suspensions is due to other factors, as, e.g., system polydispersity [28]) and electrostatic interactions [29].

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