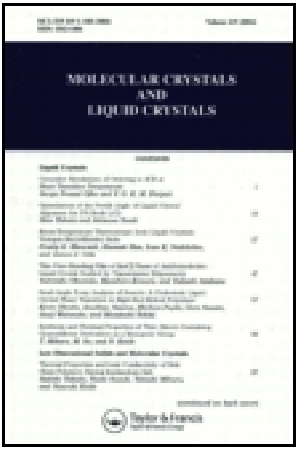

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On the Deflection and Persistence Lengths of Mesogenic Worm-Like Rods

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Persistence length is a key quantity characterizing the conformation of chain-like particles. While it is clear to interpret qualitatively as the distance over which the direction of the chain persists, its quantitative definition is not unique. Very frequently, approximate formulae are used. However, as pointed out in a recent work [P. Cifra, Polymer **45***, 5995 (2004)], their predictions are generally not correct when compared to what may be considered the exact estimate, and this especially happens for sufficiently stiff chains. The observed sensitivity of these formulae to the degree of internal flexibility of the chain has stimulated the present work, where, by employing Monte Carlo and Molecular Dynamics computer simulations, the outcomes of exact and approximate formulae are systematically studied for systems of short, semi-flexible rods which form liquid–crystalline phases. While the approximate expressions give consistent results for the isolated chain, their predictions differ in bulk ordered phases. Moreover, compared to the exact expression, the approximate formulae perform overall quite bad. Thus, if the usage of the approximate formulae is questionable in general, it is more so in the particular case of liquid–crystal phases. For mesogenic worm-like rods, another characteristic length was put forward, the deflection length. It was phenomenologically defined as the distance along the chain over which the chain behaves as isolated. It is illustrated how it can be readily evaluated from the exact definition of the persistence length.*

Keywords: computer stimulation; flexible particles; lyotropic liquid crystals

I. INTRODUCTION

Particles with only repulsive, steric interactions are basic models with which to study condensed matter systems [1]. If the particles are anisometric, besides the usual crystalline and isotropic phases, liquid–crystalline mesophases may appear in the phase diagram. Indeed, it was first pointed out by Onsager [2], and later confirmed

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by computer simulations [3], that the anisometric shape is the sole basic requirement for the formation of nematic, smectic and columnar phases. While this holds for every type of liquid–crystalline system, repulsive rods and discs are particularly good models for colloidal, lyotropic liquid crystal suspensions. Real particles forming such suspensions can be of different origin: rodlike virus particles, as the Tobacco Mosaic and *fd* viruses [4], various (bio)polymers, as DNA [5], mineral particles, as nanorods [6], et cetera.

The phase behavior and properties of rigid rod-like model particle systems is rather well understood [3]. One straightforward variation of these models, which goes in the direction of making them more realistic, is to consider flexible rather than rigid rod-like particles. In fact, most of the above-mentioned real particles have an inherent internal flexibility whose degree affects their phase behavior and properties.

It is clearly of importance to quantify the “degree of flexibility” of a flexible particle. One possibility is offered by the persistence length (ℓ_P). Qualitatively, it is defined as the distance over which the local direction of the particle persists. However, quantitatively, its definition is not unique. A few formulae are frequently employed to obtain ℓ_P. In a recent work [7], it was demonstrated how, for long chain-like particles, their predictions differ, especially when the chain is sufficiently stiff. In addition, all of them are approximate, being derived assuming a coil state for the chain and therefore not a priori transferable to rod-like chains. Finally, they differ from what is considered an exact definition of ℓ_P.

This observed strong sensitivity of all these formulae to the degree of flexibility of the chain-like particle may be even more severe for those particles which are sufficiently stiff to form liquid–crystalline phases. One of the aim of this work is to systematically investigate the predictions of the different formulae, exact and approximate, for the estimate of ℓ_P for mesogenic chain-like particles, both isolated and in bulk phases. This offers the additional opportunity to investigate condensed media effect on the conformation of the chain and how they depend on the particular degree of positional and orientational order the particles have in the phase under examination. Moreover, for chain-like particles which form mesophases, another characteristic length has been introduced, namely the deflection length, ℓ_D [8]. The latter was introduced phenomenologically. In the present work, it is also shown how the above-mentioned exact method for ℓ_P can be readily used to operatively estimate ℓ_D.

To these goals, model particles formed by nine soft–repulsive spherical beads, arranged in a chain of varying stiffness, have been considered. The Monte Carlo (MC) method [10] has been used to generate a large number of configurations of isolated chains at different temperatures, while the Molecular Dynamics (MD) techniques [10] has been used to map out the phase behavior of the worm-like models considered. The persistence length has been evaluated in both cases using the various formulae, as in Ref. [7]. The data will be used to both investigate condensed matter effect on the particle conformation and assess the degree of reliability of the approximate formulae with respect to the exact expression. It is anticipated that the latter are unreliable. Thus, although certain of them might be exploited to calculate the deflection length, this possibility is illustrated only employing the exact definition of the persistence length.

The subsequent section contains the description of the worm-like model and the details of the MC and MD computations. The worm-like model will be also used to recall the above-mentioned expressions for the estimate of ℓ_P. Results are presented and discussed in Section III, while Section IV provides the conclusions.

II. THE WORM-LIKE MODEL, DETAILS OF THE CALCULATIONS, AND THE EXPRESSIONS USED TO ESTIMATE $\ell_{\mathbf{P}}$

The worm-like model considered in this work consists of a chain of nine soft–repulsive spherical beads (Fig. 1). Two contiguous beads are maintained at a fixed distance of $\ell = 0.6\sigma$, with σ the unit of length. The vectors joining two contiguous beads i and $i+1$ are labeled $\vec{l_i}$, while $\hat{u}_i$ is the unit vector associated to them.

For each triplet of successive beads, ℓ, m, n, an angular interaction, v_{lmn}, exists of the type:

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

with K the bending constant which regulates the degree of flexibility of the chain, and θ the angle formed by the two involved bonds, as

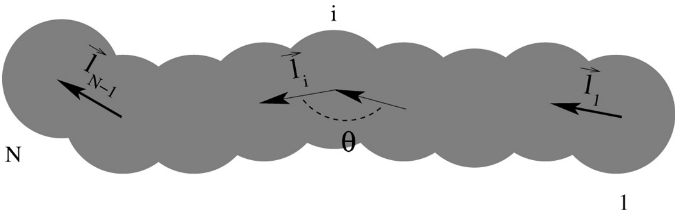


FIGURE 1 The worm-like model considered in this work, with $N = 9$.

defined in Figure 1. Thus, the minimum conformational energy of the chain corresponds to the perfectly linear conformation. Within the same chain, and with the exclusion of two contiguous beads, an interaction of the truncated and shifted Lennard-Jones type exists between two beads, i and j:

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

with u_{ij} the interaction potential energy, r the distance separating the two beads, and ϵ the unit of energy. Equation 2 regulates also the interaction between any two beads belonging to different particles, so that the total pairwise particle interaction is the sum of 81 bead-bead interactions.

In the present work, both isolated chains and collections of 600 chains will be considered for two values of K, 5556ϵ and 278ϵ.

With the help of the MC method, configurations of an isolated chain have been generated at several reduced temperatures $T^* = k_B T/\epsilon$ with k_B the Boltzmann's constant. Each configuration has been generated from the previous one according to the following procedure. One of the seven internal beads has been selected at random; for example, j. Then, all the bond unit vectors from $\hat{u}_j$ to $\hat{u}_8$ are rotated of a random selected angle around a random selected axis of the laboratory frame of reference. The total energy, angular plus non-covalent, of the new configuration is calculated and the Metropolis criterion applied.

Vice versa, two series of MD simulations have been used to trace the phase behavior of a collection of worm-like rods characterized, respectively, by the above-mentioned values of K. Several temperatures have been considered, while the reduced pressure, $P^* = P\sigma^3/\epsilon$ has been maintained at the constant value of 24.716, as in previous work [9]. Pressure and temperature have been regulated with the Nosé—Hoover method [10]. 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 and arranged in a cuboidal computational box in a hexagonal closed packed fashion. Simulations at successive temperatures were started from a well-equilibrated configuration coming from the previously considered, lower temperature. 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 $2.81 \times 10^{-4} t^*$, with $t^* = (m/\epsilon)^{1/2}\sigma$.

The phase behavior and properties of systems of worm-like rods with varying degree of internal flexibility will be reported extensively elsewhere. Here, it suffices to say that the stiffer worm-like rod system exhibits both smectic A and nematic phases in between crystalline and isotropic ones, while the more flexible rods only give rise to a nematic phase in between the crystalline and isotropic ones.

One of the aim of this work is to study systematically the predictions of the various expressions used to estimate the persistence length. The approximate expressions will be confronted together in the isolated chain case and condensed phases, as well as compared to the exact definition of ℓ_{P}. All these expressions are recalled below.

One approximate expression to estimate ℓ_P is the following:

$$\ell_P = \frac{\ell}{1 - \langle \cos\theta \rangle}, \tag{3}$$

with $\langle\rangle$ meaning a statistical average over bond angles, particles and configurations. The second involves the decay of the correlation function of the orientation of the bonds along the chain, assuming an exponential behavior:

$$\langle \hat{u}_{i+j}\hat{u}_i \rangle = \exp(-j\ell/\ell_P) \tag{4}$$

where the statistical average is intended over i, particles and configurations. Finally, the persistence length can be deduced from the average end-to-end distance of the chain, $\langle R^2 \rangle$ by exploiting the formula:

$$\langle R^2 \rangle = 2\ell_P L_c - 2\ell_P^2(1 - \exp(-L_c/\ell_P)) \tag{5}$$

with L_c the contour length, equal to 4.8σ in the present work.

It is worth noticing that all the above formulae were derived in the context of polymer physics for a chain in the coil regime and gives ∞ for the perfectly rigid rod limit [7]. The latter result should be looked at with suspicion as, if the persistence length is the distance along the chain over which the orientation persists, its maximal value should be the contour length L_c.

Indeed, the fourth expression considered satisfies this limit and has been quoted as the exact estimate of ℓ_p [7]. It is:

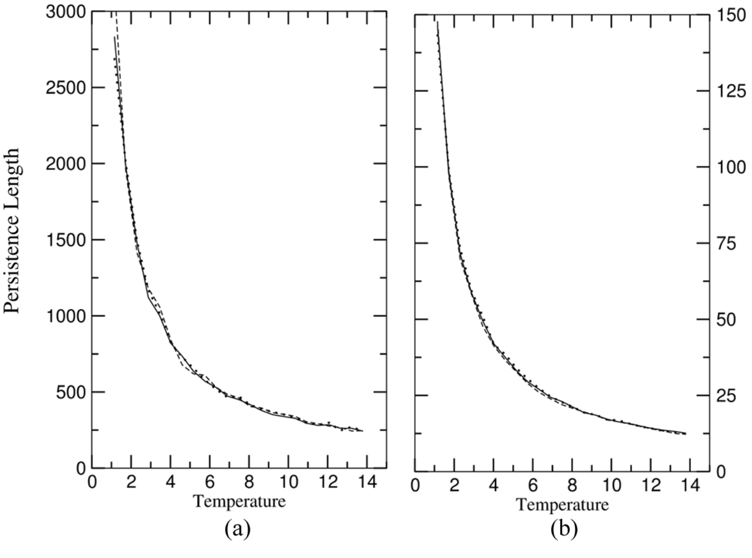
$$\ell_P = \left\langle \sum_{i=1}^{N-1} \vec{l}_i \vec{l}_1 \right\rangle \Big/ \ell \tag{6}$$

which, besides taking the limit $\ell_P = L_c$ for perfectly rigid rods, takes also the correct limit $\ell_P = \ell$ for extremely flexible chains.

III. RESULTS AND DISCUSSION

Firstly, the predictions of Eqs. (3–5) are compared together in the isolated chain case and bulk phases. While in the former case, all three approximate expressions are consistent for both values of K investigated, as it is shown in Figure 2, differences appear among these expressions when bulk phases are considered, especially at low temperatures where positionally ordered phases are present (Fig. 3). The three formulae only give the same value of ℓ_P when the worm-like rods are in the isotropic phase. The differences among the results of the approximate formulae are more marked as the bending constant and/or the temperature decrease. Generally, Eq. (3) gives the smallest value of ℓ_P, while Eq. (4) the largest. Moreover, the persistence length predicted by these formulae significantly exceeds the rod contour length, and this even in the isotropic phase of the most flexible rods.

Figure 4 gives the values of persistence length as evaluated from Eq. (6), both for the isolated chain and for chains in the bulk phases. Being characterized by well-defined limits, Eq. (6) is particularly suitable to study the effects exerted by the condensed medium on the conformation of a worm-like rod, a subject only rarely investigated



(a) (b)

FIGURE 2 Persistence length of an isolated worm-like rod evaluated for $K = 5556\epsilon$ (a) and $K = 278\epsilon$ (b) using Eq. (3) (solid line), Eq. (4) (dashed line) and Eq. (5) (dotted line). Both persistence length and temperature are in reduced units, that is, respectively, in units of σ and k_BT/ϵ.

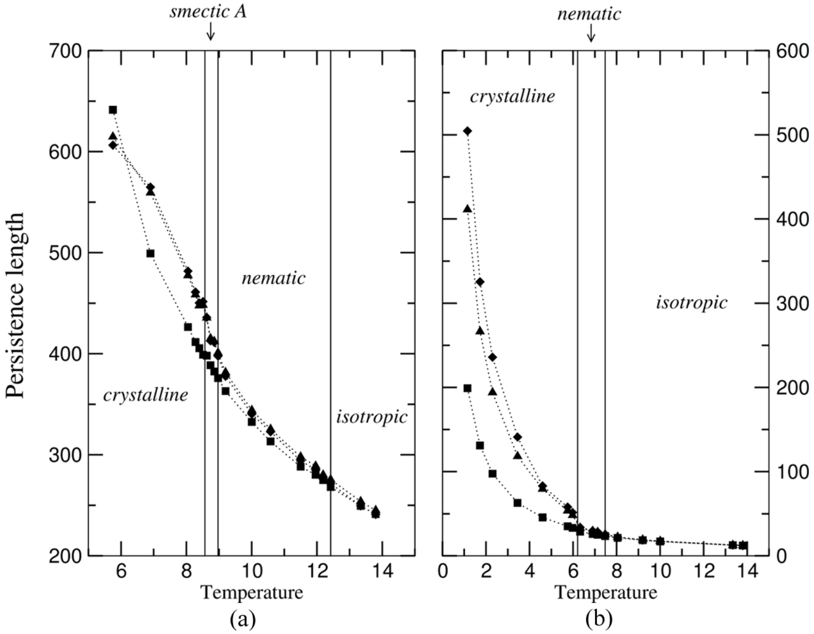


FIGURE 3 Persistence length of a worm-like rod in the bulk phases evaluated for $K = 5556\epsilon$ (a) and $K = 278\epsilon$ (b) using Eq. (3) (squares), Eq. (4) (diamonds) and Eq. (5) (triangles). Both persistence length and temperature are in reduced units, that is, respectively, in units of σ and k_BT/ϵ.

up to date [11]. For the stiffer rods, the conformation of the chains is unaltered with respect to the isolate case either at sufficiently low temperature, with the rods in a crystalline phase, or at high enough temperature, with the rods in the isotropic phase. This happens because either the temperature is so low that only conformation of very small energy are important even in the isolated case, or because the phase is isotropic, so that the liquid–crystal field is averaged to zero. On increasing the temperature, when T^* is sufficiently high and circa equal to 6, packing effects start to be observable, being the persistence length in the bulk larger than in the isolated chain case. The difference between the two values of persistence length reaches its maximum value in the successive interval of temperatures, [7.5; 8.5], until the system undergoes a transition to a smectic A phase. In the small interval of temperatures where the latter phase is stable, the persistence length has a relatively considerable drop, as can be appreciated in the inset of Figure 4. This decrease is suddenly

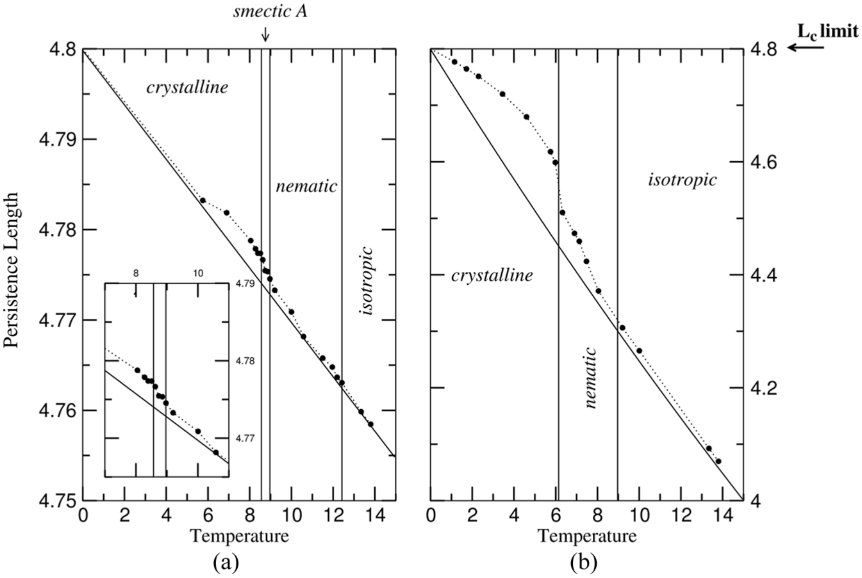


FIGURE 4 Persistence length of the worm-like rods in the isolated (line) and bulk phases (symbols); panel (a) refers to $K = 5556\epsilon$, with the insect showing details on the region where the smectic A phase is stable, while panel; (b) refers to $K = 278\epsilon$. All data have been computed using Eq. 6. Both persistence length and temperature are in reduced units, that is, respectively, in units of σ and $k_B T/\epsilon$.

counterbalanced by the transition to a nematic phase. While naturally still decreasing with temperature, the persistence length in the nematic phase does so at a smaller rate than in the smectic A phase. The fact that persistence length decreases with temperature more rapidly in the smectic A phase than in the crystalline and nematic ones may be associated to the large interdigitation of the worm-like rods between two contiguous layers which is peculiar of the smectic A phase [12]. On increasing further the temperature, the nematic phase becomes unstable with respect to the isotropic phase. In the latter phase, the values of ℓ_P come back to being very close to the respective values in the isolated chain cases.

Similar considerations also hold for the system composed of more flexible rods, with the difference that the latter no longer exhibits a smectic A phase and that the differences between the values of ℓ_P in the bulk and in the isolated chain case are clearly more marked. Worth to be noticed is the drop of the persistence length at the crystalline-nematic phase transition. In the nematic phase, ℓ_P decreases more gently, until the system approaches and reaches the isotropic phase where, again, condensed matter effects are very modest.

These results are in accordance with the earlier observation made in Ref. [8], where the concept of deflection length is discussed. In an anisotropic environment, any worm-like rod experience the interaction of the mean-field created by its neighbors. This forces the worm-like rod to adopt a straighter configuration than it would be if it were isolated. On the basis of the results presented above, it would appear that the smectic A phase is less efficient in conferring the rod a linear configuration, the persistence length in this phase decreasing with the largest rate. The interactions of the neighboring particles become effectively operative at ℓ_D, where the liquid–crystalline field deflects the chain back. For distances smaller than ℓ_D, the conformational statistics of the chain is more or less equal to that of the unconfined chain. This leads to the following operative definition of ℓ_D, as the distance along the chain for which the quantity ℓ_J,

$$\ell_J = \left\langle \sum_{i=1}^{J-1} \vec{l}_i \vec{l}_1 \right\rangle \Big/ \ell, \tag{7}$$

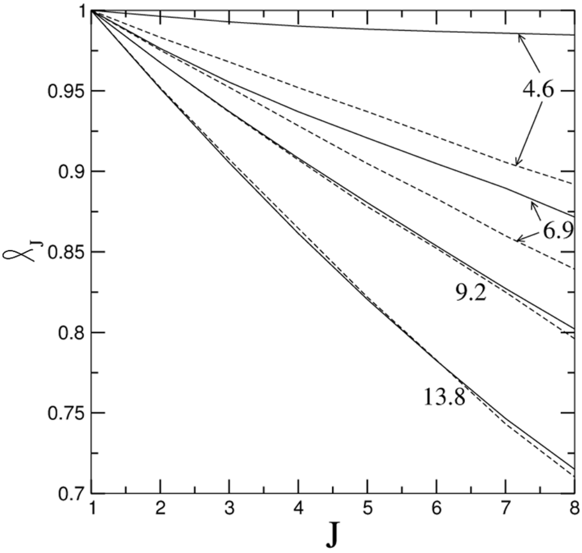


FIGURE 5 Decay of the function ℓ_J *versus* J for the systems with bend constant $K = 278$ and at indicated temperatures. Solid lines correspond to the bulk phases while dashed lines to the isolated phases.

evaluated in the bulk phase, becomes significantly different from the analogous quantity in the isolated phase. Thus, the deflection length can be extracted by plotting ℓ_J *versus* J for both bulk and isolated phase. This is illustrated in Figure 5, where ℓ_J is plotted as a function of J for the case of $K = 278$ at various temperatures. At the lowest temperature considered, the two curves corresponding to the bulk and isolated chains immediately depart one from the other and ℓ_D can be identified with the bond length ℓ. At the successive temperatures considered, the decay of the two respective curves is consistent with a value of ℓ_D of 2ℓ, 4ℓ and 6ℓ, respectively. Naturally, the trend of ℓ_D parallels the behavior of the difference of ℓ_P in the bulk phase and in the isolated chains, given in Figure 4.

IV. CONCLUSIONS

Systems of semi–flexible rods with varying degree of internal flexibility have been considered. Two particular cases have been given attention: in one case, the rods are quite stiff, while in the other the rods are more flexible. Monte Carlo computer simulations have been carried for the isolated worm-like rods. Molecular Dynamics computer simulations have been carried out for bulk systems. In the stiffer case, the phase behavior comprises crystalline, smectic A, nematic and isotropic phase on increasing temperature, while in the more flexible case, the intermediate smectic A phase is no longer stable and the nematic phase is present in a narrower interval of temperatures than in the case of stiffer rods.

The trajectories generated during these simulations have been used to calculate the persistence length of the worm-like rods. Three common approximate expressions, as well as the exact definition of the persistence length, have been employed. It has been found that the approximate relationships, while giving consistent results in the isolated case as well as the bulk isotropic phase, provide different predictions in the bulk ordered phases. In addition, they give numbers significantly higher than the exact estimate, even in the isotropic phase. Thus, these approximate expressions should not be used to estimate persistence length of mesogenic worm-like rods.

The exact estimate is particularly useful to investigate condensed matter effects. It has been found that these are active in the ordered phases, being the persistence length in the isotropic phase equal to that in the isolated chain at the same temperature. More novelly, it has also been found that in the smectic A phase the persistence length decreases with temperature with a larger rate than in both crystalline and nematic phase. These results can be traced back to the concept of deflection length. It has been illustrated how the latter characteristic length can be extracted exploiting the exact definition of persistence length.

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