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Short Communication

Flexible polymers in a nematic medium: a Monte Carlo simulation

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Abstract. — Monte Carlo simulations of self-avoiding random walks surrounded by aligned rods on a square lattice and a simple cubic lattice were performed to address the topological constraints involved for dilute solutions of flexible polymers in a highly oriented nematic solvent. The nematic constraint exerted by the solvent is modelled by requiring that the distance between nearest neighbour chain segments in the direction of the director of the nematic solvent is such that a discrete number of rods, representing the perfectly ordered nematic solvent, fits exactly in between. Rod lengths of one or two lattice spacings are used. In this case interesting scaling behaviour for the radius of gyration and the end-to-end distance is found. Perpendicular to the director the coil behaves as a two- (or one- in the case of a square lattice) dimensional self-avoiding walk, whereas parallel to the director it behaves as a random walk. The conformations have a disk-like shape with the radius of gyration perpendicular to the director being considerably larger than the parallel component. These simulations address only one aspect of flexible polymers in nematic solvents. In reality the presence of the coil also reduces the entropy of the solvent which has exactly the opposite effect on the shape of the polymer coil.

Introduction.

An interesting area of polymer physics concerns the size and shape of polymer coils in an anisotropic environment. A simple example is a dilute polymer solution confined between two parallel plates. In this case the intrinsic anisotropic conformation of the coils interferes with the spatial constraint. When the distance between the plates is reduced, the coil first orientates with its two largest axes parallel to the plates. The deformation of the polymer coil only starts when the distance is comparable to the span length in the direction associated with the shortest axis [1].

A nematic solvent constitutes another example of an anisotropic environment for the dissolved polymer. Experimentally, the conformations of flexible polymer coils in a nematic solvent were studied by NMR and small-angle neutron scattering (SANS). NMR gives information on
the local order, whereas the global orientation of the coil, described by the square radii of
gyration parallel, \( S_{ll}^2 \), and perpendicular, \( S_{ll}^2 \), to the director of the nematic solution can be
found by SANS [2]. Besides these microscopic techniques, the global orientation of the coils
has also been investigated by viscosity measurements, interpreting the results on the basis of
a model presented by Brochard [3-5]. The interesting point is that under certain conditions
the polymer coil appears to be elongated parallel to the director of the nematic solvent. At
first sight this situation resembles that of a polymer coil confined between two parallel plates,
suggesting that also here the effect is merely an orientation of the anisotropic shaped coil [6].
This observation prompted us to study the shape of a polymer coil in a nematic solvent, using
lattice simulations.

So far the experimental results for (semi-)flexible chains in a nematic environment have been
interpreted using theories in which a mean-field potential is introduced. The potential models
the coupling of the nematic field with the chain. [7-14]. However, the effect of the excluded
volume has been largely ignored. The Monte Carlo simulations for lattice chains, reported
here, are explicitly undertaken to address this aspect. In these simulations the nematic solvent
molecules are modelled as rods aligned perfectly parallel to the director. Therefore, it is obvious
that the relevance of our simulation is limited to a temperature regime far below the critical
temperature for the nematic to isotropic phase transition of the solution.

**Simulation method.**

Monte Carlo simulations of self-avoiding random walks (SAW) representing the flexible poly-
mer, on a 100 \( \times \) 100 \( \times \) 100 simple cubic or 100 \( \times \) 100 square lattice were performed. The lengths
\( N \) of the lattice chains considered, were 24-149 steps. A step is defined as a lattice vector
connecting two lattice points occupied by connected chain segments; so a chain of \( N \) steps
comprises \( N + 1 \) segments. One of the lattice axes is chosen to be parallel to the director of
the nematic rods. The number of chain conformations is restricted by a nematic constraint.
The constraint is modelled by requiring that the distance between nearest-neighbour segments
in the direction of the director (here the \( z \) axis) is such that a discrete number of rods fits
exactly in between (Fig. 1). It resembles, but differs in an essential way from the model of
SAW's on a lattice in a field of fixed asymmetric obstacles studied by Baumgärtner et al. [15]
and DiMarzio [16]. Conformational averages of quantities \( A \) are calculated as

\[
\langle A \rangle = \frac{1}{n} \sum_{i=1}^{n} A_i
\]

(1)

where the angular brackets indicate a conformational average, \( i \) is the conformational index
and \( n \) the total number of conformations.

The reptation algorithm is used to generate different SAW conformations. The first 400,000
attempted moves after completion of chain growth were ignored. From the subsequent interval
of 40,000-400,000 attempted moves the quantities of interest were calculated each time a
conformation satisfying the nematic constraint was obtained. This procedure was repeated for
at least seven independent runs. After averaging again, the statistical errors were calculated
as usual from the averages per run. We were able to generate reliable results for chain lengths
up to \( N = 150 \). During the simulations the segments were at regular intervals rotated over an
angle of 90° around one of the randomly chosen orthogonal lattice axes with the origin of the
coordinate system in the centre of the lattice. The centre of mass of the SAW is maintained
near this origin by a translation of the whole conformation when necessary. This rotation
ensures a more efficient sampling of the relevant part of the configuration space (a kind of pivot algorithm) [17].

Results and discussion.

The averages for the radius of gyration parallel, \( \langle S^2_\parallel \rangle = \langle S_x^2 \rangle \) and perpendicular, \( \langle S^2_\perp \rangle = (\langle S_x^2 \rangle + \langle S_y^2 \rangle) / 2 \), to the director, and the corresponding mean-square end-to-end distances, \( \langle R_\parallel^2 \rangle \) and \( \langle R_\perp^2 \rangle \), were calculated for the square and simple cubic lattice. Two different lengths of the rods, one and two lattice spacings long, were chosen. The scaling exponents for the square radii of gyration and for the square end-to-end distances were obtained by linear regression according to

\[
(\ln (A_i)) = \ln (C_i) + 2\nu \ln (N)
\]

where \( A_i \) is now the parallel or the perpendicular component of the square radius of gyration or square end-to-end distance. Since the scatter in the data used for linear regression is comparable, only one characteristic example is shown in figure 2.

A typical chain conformation is shown in figure 1. Results are presented in tables I and II. For all chain lengths considered the perpendicular component of the radius of gyration, and the end-to-end distance is larger than the parallel one. Moreover, these results show that a chain subjected to a nematic constant on a simple cubic of square lattice behaves as a SAW in the plane, resp. on the line, perpendicular to the director, and as a random walk in the parallel direction. The SAW scaling exponents are the Flory exponent, \( \nu_F \), for a spatial dimension \( d' = d - 1 \), \( d \) being the lattice dimension considered. Hence,

\[
\langle A_\perp \rangle \sim N^{2\nu_F}, \quad \nu_F = \frac{3}{d' + 2} = \frac{3}{d + 1}
\]

It is also clear that the values of the scaling exponents are within error independent of the lengths of the rods. This result can be easily understood on the basis of a characteristic conformation like the one presented in figure 1. A disk-like conformation with its largest
Fig. 2. — Double logarithmic plot for determination of critical exponents, for a SAW on a simple cubic lattice: (●) $<\ln (S^2_\perp)>$; (○) $<\ln (S^2_\parallel)>$. Length of rods is one lattice spacing. Maximum relative error is 0.04.

Table I. — Scaling exponents.

<table>
<thead>
<tr>
<th>lattice</th>
<th>rod length$^*$</th>
<th>$S^2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$2\nu_\perp$</td>
<td>$2\nu_\parallel$</td>
</tr>
<tr>
<td>square</td>
<td>1</td>
<td>1.94 ± 0.02</td>
<td>1.09 ± 0.03</td>
</tr>
<tr>
<td>cubic</td>
<td>1</td>
<td>1.44 ± 0.05</td>
<td>0.93 ± 0.05</td>
</tr>
<tr>
<td>cubic</td>
<td>2</td>
<td>1.44 ± 0.03</td>
<td>1.03 ± 0.02</td>
</tr>
</tbody>
</table>

$^*$ unit of length is one lattice spacing

Table II. — Average size.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$S^2_\perp$</th>
<th>$S^2_\parallel$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.5</td>
<td>2.5</td>
<td>0.03</td>
</tr>
<tr>
<td>50</td>
<td>8.4</td>
<td>4.7</td>
<td>0.009</td>
</tr>
<tr>
<td>75</td>
<td>14.1</td>
<td>7.3</td>
<td>-0.001</td>
</tr>
<tr>
<td>100</td>
<td>22.9</td>
<td>9.4</td>
<td>-0.016</td>
</tr>
<tr>
<td>125</td>
<td>31.0</td>
<td>10.0</td>
<td>-0.013</td>
</tr>
<tr>
<td>150</td>
<td>43.0</td>
<td>13.0</td>
<td>-0.004</td>
</tr>
</tbody>
</table>

dimensions perpendicular to the director suffers the least from the constraint. A more isotropic conformation is far less probable. The essential feature is that back folding in the direction perpendicular to the director is strongly hampered. In the model, the influence of the excluded-volume effect in the direction parallel to the director is nullified due to the strongly enhanced excluded-volume effect in the directions perpendicular to the director. For two dimensions, the situation is identical to that found for directed SAW’s, and the SAW here is apparently in the
same universality class [18, 19]. Another quantity of interest is the order parameter $s$ defined as

$$s \equiv \frac{3}{2} \frac{\langle N_{||} \rangle}{N} - \frac{1}{2} \quad \text{for} \quad d = 3$$

$$s \equiv 2 \frac{\langle N_{||} \rangle}{\langle N \rangle} - 1 \quad \text{for} \quad d = 2$$

where $N_{||}$ is the number of steps parallel to the director. Despite the global anisotropy as indicated by the scaling behaviour discussed above, and the corresponding flat shape no local ordering is observed ($s = 0$, Tab. II).

The foregoing results show that as long as the solvent entropy is ignored, the nematic constraint favours a disk-like shape with the longest dimension perpendicular to the director. This result suggest a behaviour that is counter intuitive. Now, the analysis so far clearly shows why backfolding in a direction perpendicular to the director is hampered. However, as far as the application to real systems is concerned an important factor favouring the exact opposite behaviour is missing. If a segment of the SAW is present, the degeneration of the solvent configuration on the line parallel to the director containing this segment disappears, i.e. the configuration is uniquely defined now (Fig. 3). If only these entropic losses of the solvent are considered, disk-like conformations become extremely unfavourable. Hence, in reality we are dealing with at least two opposing effects and the outcome is unclear. Since, both effects amount to a reduction in the overall entropy it is not surprisingly to find total immiscibility of flexible polymers in nematic low molecular weight liquid crystals in the limit of long chain lengths [32].

![Diagram](image.png)

Fig. 3. — a) Illustration of the twofold degeneracy of the solvent configuration on a line parallel to the director in the absence of a polymer segment. b) Illustration of the uniquely defined solvent configuration on a line parallel to the director in the presence of a polymer segment. (●-●) chain segment, (○-○) rod.

Several experimental techniques like NMR, small angle X-ray scattering (SAXS), SANS or viscosity measurements have been used to measure conformational properties of flexible polymers in a nematic medium. Our results could be relevant for very dilute solutions of flexible polymers in a nematic solvent at temperatures sufficiently far below the nematic-isotropic transition temperature, with only a slight interaction between polymer and solvent.
This situation was denoted the "weak coupling regime" by Brochard [20, 21], in contrast with the "strong coupling regime", which is characterized by a local destruction of the nematic order by the chains. The latter situation prevails near the nematic-isotropic transition temperature of the mixture. An example of the former kind of system is a dilute solution of polystyrene in the nematic solvent N-(p-ethoxy-benzylidene)-p-butylaniline (EBBA). The global chain shape and the local-order parameter of this solution were determined by acoustic measurements and NMR, respectively. It was found that the hydrodynamic radius of the chain perpendicular to the director of the solution increases strongly when the temperature decreases while on the other hand the local order parameter of the polymer is very small and shows only a very slight increase. The authors actually concluded, that if the weak coupling regime applies, the polymer coils would go to a flat disc as the temperature decreases [2-4].

A different, but in certain aspects comparable, situation arises for flexible polymers with mesogenic groups joined to the polymer backbone by a flexible spacer. The backbone shows similar global and local ordering in a nematic environment created by the side groups, when the length of the flexible spacer between the backbone and the mesogenic group is not too short. Then the conformations of the polymer backbone are supposed to be more or less independent from the side groups [22]. SANS experiments on polymetacrylates with mesogenic units joined to a deuterium labeled backbone by an alkyl spacer, showed that the backbone assumes a flat conformation in the nematic melt \( S^2_\perp > S^2_\parallel \), and that moreover this difference increases with a decrease in temperature [23-27]. This is not surprising, since the order of the mesogenic groups probably increases with a decrease in temperature, thus enhancing the flatness of the backbone conformation.

Concluding remarks.

The average shape of flexible polymers in a nematic solvent is the result of a delicate balance between anisotropic enthapic and entropic effects. The simulations show that the anisotropic excluded-volume effect favours a flat disc-like shape of the SAW. The introduction of the flexible polymer in the nematic solvent reduces the entropy of the solvent. With the present model this cannot be taken into account accurately, since most conformations that satisfy the "nematic constraint" have a disk-like shape and therefore an extremely small weight factor in the partition function due to the corresponding large reduction in solvent entropy. Still, our results suggest that local destruction of the nematic order by the polymer is not the only possible explanation for the absence of anisotropy in systems like polystyrene in p-azoxyanisole [2]. If, however, favourable enthalpic interactions exist between the nematic solvent and the polymer segments (as for a main-chain nematic polymer in p-azoxyanisole) the shape of the coil is likely to be stretched along the director below the nematic-isotropic transition point [6, 28-31].

References