Вікторія Богданівна Блавацька
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Конформаційні переходи в напівгнучких полімерах: числові симуляції

Роботу отримано 15 лютого 2011 р.

Затверджено до друку Вченою радою ІФКС НАН України

Рекомендовано до друку відділом статистичної теорії конденсованих систем

Виготовлено при ІФКС НАН України

Національна академія наук України

ІНСТИТУТ
ФІЗИКИ
КОНДЕНСОВАНИХ
СИСТЕМ

ICMP–11–01E

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CONFORMATIONAL TRANSITIONS IN SEMIFLEXIBLE POLYMERS: NUMERICAL SIMULATIONS

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ЛЬВІВ

УДК: 538.91

PACS: 36.20.-r,07.05.Tp,05.40.Fb

Конформаційні переходи в напівгнучких полімерах: числові симуляції

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Анотація. Ми досліджуємо конформаційні властивості напівгнучких полімерів в рамках граткової моделі випадкових блукань без самоперетинів (self-avoiding walks – SAW) із енергією згинання ε, залежною від взаємоорієнтації послідовних кроків. Застосовується алгоритм Розенблюта із збідненням та збагаченням (PERM). Аналізуються випадки, коли згини енергетично вигідні ($\varepsilon < 0$) та невигідні ($\varepsilon > 0$), і обговорюються деталі переходу "клубок-стержень" та переходу в "надгнучкий" стан.

Conformational transitions in semiflexible polymers: numerical simulations

V.Blavatska, K.Haydukivska, Yu.Holovatch

Abstract. We study the conformational properties of semiflexible polymers within the lattice model of self-avoiding random walks (SAW) with bending energy ε dependence on orientation between successive steps. We apply the pruned-enriched Rosenbluth method (PERM). Both the cases of bending preference ($\varepsilon < 0$) and unfavorableness ($\varepsilon > 0$) are analyzed, and details of "coil-to-rod" transition as well as transition into the "superflexible" state are discussed.

Подається в Українського фізичного журналу
Submitted to Ukrainian Journal of Physics

1. Introduction

Many polymers in chemical and biological physics are characterized by linear chemical architecture and thus behave as flexible chains. Typical examples of flexible polymers are synthetic polymers with a carbon backbone, such as polyethylene, where the carbon bonds along the backbone can easily rotate against each other. The statistical properties of flexible polymers under good solvent conditions are thoroughly studied by now [1,2]. In particular, it was found, that typical long flexible polymer chains in good solvents form crumpled coils with the size measure such as mean-squared end-to-end distance $\langle R^2\rangle$ obeying the scaling law with the number of monomers N:

$$\langle R^2\rangle \sim N^{2\nu}, \tag{1}$$

where ν is a universal exponent, depending on space dimension d only ($\nu(d=3) = 0.5882 \pm 0.0011$ [3]).

Recently, much interest was paid to semiflexible polymers, mostly since important biopolymers such as DNA and some proteins belong to this class [4,5]. Typically, these polymers are supramolecular assemblies with a relatively large monomer diameter. Also some synthetic polymers exhibit some stiffness over short distances along the chain. The competition between thermal energy and the bending energy of the polymer sets a characteristic length scale, the persistence length l_p.

The theoretical efforts to properly include the stiffness of the chain into calculations, including so-called wormlike chain model [6,7], have not succeeded, however, in incorporating the exclude-volume effects fully. Halley et al. [8] proposed to treat the problem of semiflexible polymers in the language of lattice model of biased self-avoiding walks (BSAW) with different statistical weights for "trans" steps (straight joins between two neighbour monomers) and "gauche" steps (those leading to bending of a polymer chain). The persistence length was thus introduced as inversely proportional to probability of a "gauche" step, and the scaling form for $\langle R^2\rangle$ was proposed:

$$\langle R^2\rangle = N^2 f\left(\frac{N}{l_p}\right). \tag{2}$$

Here, $f(N/l_p)$ is the scaling function, describing crossover between two main regimes: on the chain length much larger than l_p, any polymer behaves as a flexible chain obeying scaling law (1), whereas for the chain length much smaller then the persistence length, the polymer attains the limit of a rigid rod with $\langle R^2\rangle \sim N^2$. The scaling properties of BSAW were studied both numerically [9–14] and within analytical approaches [15–17].

A slight modification of BSAW model was proposed by Giacometti and Maritan [18] by introduction a bending energy ε associated to each step away from the direction of the previous step, so that each "turn" of trajectory is associated with statistical weight $\mathrm{e}^{-\varepsilon}$ (see Fig. 1). The case when $\varepsilon \gg 0$ corresponds to stiff chain limit, whereas at $\varepsilon \ll 0$ the bends become energetically favorable and very fuzzy "superflexible" chains having a turn associated at each step appear. Whereas the former limit is deeply related to "coil-to-rod" transition mentioned before, less is known about the latter case, when bending is favorable. In particular, an interesting question about the typical shape of such a "super-flexible" polymer chain is still unresolved.

In the present paper, we consider the lattice model of semiflexible polymers with bending energy ε, distinguishing the stiff and flexible limits. Applying numerical simulations, we evaluate the explicit bending dependence on the parameter ε and analyze the properties of "superflexible" state.

2. The method

To study the configurational properties of self-avoiding random walks on the regular lattice, we use the pruned-enriched Rosenbluth method

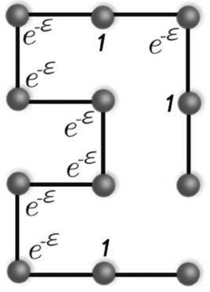

Figure 1. The schematic presentation of SAW trajectory in $d = 2$ with bending energy ε associated with each turn. The number of bends ("gauche"-steps) equals 7. The bending energy $\varepsilon = 0$ is implied at each straight join ("trans"-step).

(PERM) [19], combining the original Rosenbluth-Rosenbluth algorithm of growing chains [20] and population control [21]. Each n-th monomer is placed at a randomly chosen neighbor site of the last placed $(n-1)$th monomer ($n \leq N$, where N is total length of the polymer). If this randomly chosen site is already visited by a chain trajectory, it is avoided without discarding the chain and a weight W_n is given to each sample configuration at the nth step:

$$W_n = \prod_{l=1}^{n} m_l \mathrm{e}^{-\varepsilon_l(1-\cos\theta_l)}, \tag{3}$$

where m_l is the number of free lattice sites to place the lth monomer, θ_l is an angle between steps l and $l-1$ and ε_l is a bending energy of lth step orientation different relating to the preceding step (corresponding to the case $\theta = \pi/2$.)

The growth is stopped when the total length N of the chain is reached (or, at $n < N$, the "dead end" without possibility to make the next step is reached), then the next chain is started to grow from the same starting point.

The configurational averaging for any quantity of interest then has the form:

$$\langle(\ldots)\rangle = \frac{1}{Z_N}\sum_{k=1}^{M} W_N^k(\ldots), \quad Z_N = \sum_{k=1}^{M} W_N^{\mathrm{k}}, \tag{4}$$

where the summation is performed over the ensemble of all constructed N-step SAWs ($M \sim 10^5$ in our case).

The weight fluctuations of the growing chain are suppressed in PERM by pruning configurations with too small weights, and by enriching the sample with copies of high-weight configurations. These copies are made while the chain is growing, and continue to grow independently of each other. Pruning and enrichment are performed by choosing thresholds $W_n^<$ and $W_n^>$, which are continuously updated as the simulation progresses. If the current weight W_n of an n-monomer chain is less than $W_n^<$, the chain is discarded with probability 1/2, otherwise it is kept and its weight is doubled. If W_n exceeds $W_n^>$, the configuration is doubled and the weight of each identical copy is taken as half the original weight. Otherwise, the chain is simply continued without enriching or pruning the sample.

For updating the threshold values we apply similar rules as in [22,23]: $W_n^> = C(Z_n/Z_1)(c_n/c_1)^2$ and $W_n^< = 0.2W_n^>$, where c_n denotes the number of created chains having length n, and the parameter C controls

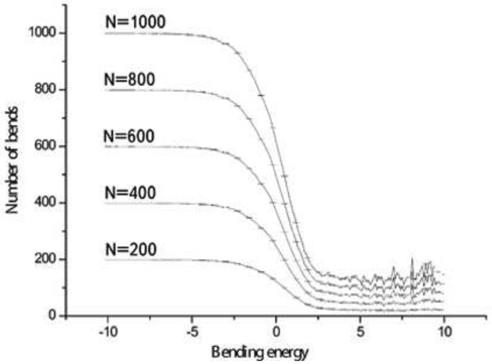

Figure 2. Number of bends in the polymer chain as a function of bending energy ε at different number of monomers N in $d = 2$.

the pruning-enrichment statistics; it is adjusted such that on average 10 chains of total length N are generated per each tour [23].

3. Results and Discussion

Applying the PERM algorithm, we analyze the peculiarities of conformational transitions under varying the bending energy ε in space dimensions $d = 2$ and $d = 3$. Numerical simulations were performed for the chain length up to 1000 monomers in $d = 2$ and up to 600 in $d = 3$. The bending energy in both cases was varied in the limits $-10, \ldots, 10$.

To describe quantitatively the extent of chain flexibility or stiffness, let us evaluate the number of bends in polymer chain of length N, corresponding to the number of time when the SAW trajectory change it's direction. Figs. 2 and 3 present our simulation results. The case $\varepsilon = 0$ corresponds to the regime of flexible polymer coil with averaged size measure given by Eq. (1). For negative values of ε, the bendings becomes more and more favorable. In the limit $\varepsilon \ll 0$ we receive the "superflexible" polymer chain with turning at each step, so that the the number of bends equals $N - 1$ for an N-step SAW. In both 2 and 3 dimensions, we can estimate the marginal value of $\varepsilon \simeq -3.5$, below which the conformational transition to "superflexible" state occurs. For positive ε, when each bending of a trajectory gain an energy penalty, the limit of completely stiff rod-like polymers should be gradually approached. The limitations of our method, however, enable to catch this tendency only for rather short chain length $N \leq 100$.

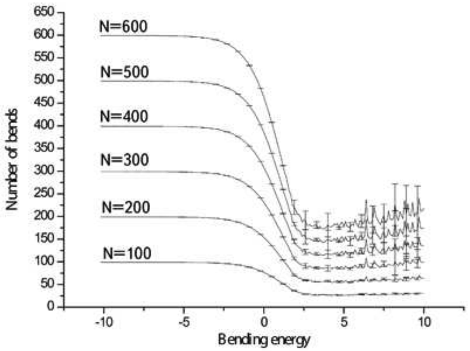

Figure 3. Number of bends in the polymer chain as a function of bending energy ε at different number of monomers N in $d = 3$.

Whereas in the most of previous investigations the behavior of semiflexible polymers under increasing stiffness (corresponding to the case $\varepsilon > 0$ in our model) was of interest, less attention was paid to the opposite situation of "superflexible" polymers ($\varepsilon < 0$). An interesting question

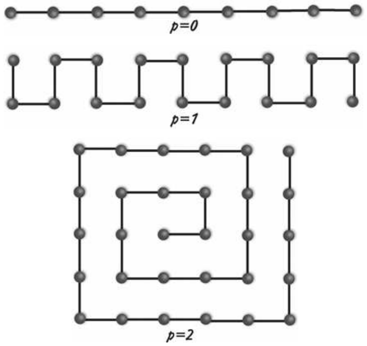

Figure 4. Schematic presentations of SAW trajectories in $d = 2$ with number of nearest neighbor contacts $p = 0$ (rod-like configuration), $p = 1$ (zigzag configuration), $p = 2$ (compact globule).

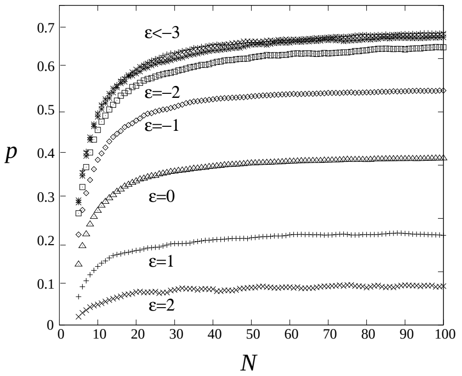

Figure 5. Number of contacts with nearest neigbours in a SAW trajectory in $d = 2$ as function of chain length N at different value of bending energy ε.

arises, what is a typical shape of such a configuration? One could in principle expect the zigzag configuration as shown in the middle of the Fig. 4.

We can shed light into this question by studying the averaged number of nearest neighbor contacts p (i.e., number of cases when two nearest neighbour sites are occupied but connected by a bond) of a typical polymer chain. It is obvious, that for completely stretched, rod-like configuration we will have $p = 0$, whereas for expected zigzag-like structure $p = 1$ (in $d = 2$), as sketched in Fig. 4. Our numerical results for p values as function of bending energy ε for SAWs in $d = 2$ are presented in Fig. 5. At $\varepsilon = 0$, corresponding to ordinary SAW problem, the value of nearest neigbour contacts in d dimensions can be estimated from the empirical relation:

$$p = 2d - 1 - z(d), \tag{5}$$

where $z(d)$ is a SAW fugacity (averaged number of possibilities to make the next step in a growing trajectory). Indeed, for a simplified case when the trajectory is allowed to cross itself (so-called Random Walks), in (hyper)cubic lattice in d dimensions it is easy to show that $z(d) = 2d$. Taking into account the self-avoidance effect, first of all the “turning back” at each step is forbidden, which reduced the fugacity to the value $2d-1$. Finally, one noticed that another factor which reduces the fugacity due to the self-avoidance effect are the nearest neighbour contacts p. Substituting in $d = 2$ the known value $z(d = 2) = 2.6385 \pm 0.0001$ [24] into (5), we receive an estimate for the ordinary SAW: $p = 0.361$. Our result for the case $\varepsilon = 0$, obtained by least-square fitting of the data gives $p = 0.354 \pm 0.009$ and is thus nicely supported.

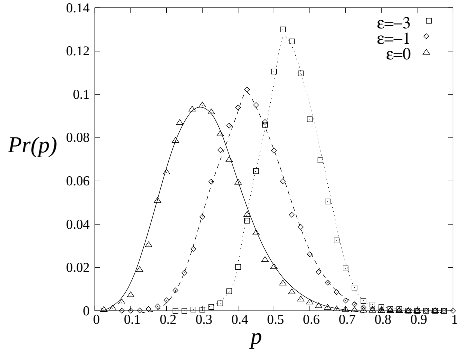

Figure 6. Probability distribution of number of nearest neighbor contacts in $N = 40$-step SAW trajectory in $d = 2$ at different values of bending energy ε.

At positive values of ε, as expected, the averaged nearest neigbour contact tends to 0. For negative ε, the p value gradually increases until we reach the already mentioned marginal value of bending energy, below which the crossover to “supeflexible” phase occurs. In this limit, we estimate $p = 0.690 \pm 0.009$, which can describe a “smeared” zigzag configuration (cf. Fig. 4). The probability distribution of p at different values of bending parameter ε is given in Fig. 6.

4. Conclusions

We studied the conformational properties of semiflexible polymers within the lattice model of self-avoiding walks with additional bending parameter ε, which is negative for “gauche” step preference (step which is not in the same direction as preceding step) and positive for “trans" step preference. An important characteristics of the the semiflexible polymers with “trans” step preference is the persistence length l_p. At scales smaller then l_p, polymer attain the limit of rigid rod, whereas on the chain length much larger than persistent length, any polymer behaves as a flexible chain consisting of independent segments of the size l_p. Another interesting case is “gauche” step preference ($\varepsilon < 0$), describing the situation when bendings are favorable and in the limit $\varepsilon \to -\infty$ a "superflexible" chain with turning at each step is predicted.

We considered the properties of both "coil-to-rod" transition and transition into "superflexible" state by studying the averaged number of bendings in typical SAW configuration as function of ε. The existence of marginal value of $\varepsilon \simeq -3.5$ is obtained, below which the polymer chain consisting of N monomers, has $N-1$ bendings and thus is in a "superflexible" state. This is also confirmed by studying the averaged nearest contact number p, which characterizes the topological properties of polymer configuration. Whereas for the polymer chain in the flexible coil regime ($\varepsilon = 0$) this value equals $p = 0.354 \pm 0.009$, it is found to increase in the bending preference case and is estimated to be 0.690 ± 0.009 at $\varepsilon \leq -3.5$.

Acknowledgments

This work was supported in parts by the grant of the Presidium of National Academy of Sciences of Ukraine (V.B.). We would like to thank the members of the seminar of Laboratory for Statistical Physics of Complex Systems and in particular R. Romanik for useful discussions.

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