

# CONFORMATIONAL PROPERTIES OF SEMIFLEXIBLE POLYMERS: NUMERICAL SIMULATIONS

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We study the conformational properties of semiflexible polymers within the lattice model of self-avoiding random walks (SAW) with bending energy  $\varepsilon$  that depends on the orientation between directions of two consecutive 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 the “coil-to-rod” transition, as well as properties of the “superflexible” state, are discussed.

## 1. Introduction

Many polymers in chemical and biological physics are characterized by a linear chemical architecture and thus behave as flexible chains. After the polymerization, a single flexible macromolecule can adopt many different conformations. By a conformation, we call the spatial structure of a polymer determined by the relative locations of its monomers [1–3]. Typical examples of flexible polymers are synthetic polymers with a carbon backbone, such as polyethylene, where the neighboring carbon atoms can easily rotate around single  $\sigma$ -bonds. The statistical properties of flexible polymers under good solvent conditions are thoroughly studied by now [4–6]. In particular, it was found that typical long flexible polymer chains in good solvents form crumpled coils with size measure such as the mean-squared end-to-end distance  $\langle R^2 \rangle$  obeying the scaling law with the number of monomers  $N$ :

$$\langle R^2 \rangle \sim N^{2\nu}, \quad (1)$$

where  $\nu$  is a universal exponent depending on the space dimension  $d$  only ( $\nu(d=3) = 0.5882 \pm 0.0011$  [7]).

Recently, much interest was paid to semiflexible polymers, mostly since many important organic macromolecules such as DNA and some proteins belong to this class [8, 9]. Typically, these macromolecules are characterized by massive side-groups (e.g., radicals of amino acids) along the carbon backbone. Usually, the

semiflexible polymers are characterized by a relatively large persistence length  $l_p$ , so that it becomes compatible with other important length scales that determine the polymer behavior. Usually, the persistence length of semiflexible polymers can reach up to one hundred nanometers (e.g., the mechanical persistence length of a DNA macromolecule is of order of 50 nm [9]). Moreover, some synthetic polymers are characterized by a stiffness over short distances along the chain (polystyrene with side phenol groups).

It is established that the spatial conformational properties of flexible polymer macromolecules in good solvents can be successfully studied within the frames of the SAW lattice model. Though the model is quite simple, it allows to obtain the high-precision estimates of some universal spatial characteristics of macromolecules. In [10], it was proposed to generalize the SAW model for the case of semiflexible polymers, introducing different statistical weights for “trans” steps (straight joins between two neighbor monomers) and “gauche” steps (those leading to a bending of the polymer chain). The persistence length of such biased self-avoiding walks (BSAW) was thus introduced as inversely proportional to the probability of a “gauche” step, and the scaling form for  $\langle R^2 \rangle$  was proposed:

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

Here,  $f(N/l_p)$  is the scaling function describing the crossover between two main regimes: on the chain length much larger than  $l_p$ , any polymer behaves as a flexible chain obeying the scaling law (1); whereas for the chain length much smaller than 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 [11–16] and within analytical approaches [17–19].

A slight modification of the BSAW model was proposed in [20] by the introduction a bending energy  $\varepsilon$

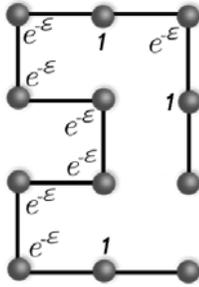


Fig. 1. The schematic presentation of a SAW trajectory in  $d = 2$  with bending energy  $\epsilon$  associated with each turn. The number of bends (“gauche”-steps) equals 7. The bending energy  $\epsilon = 0$  is implied at each straight join (“trans”-step)

associated to each step away from the direction of the previous step, so that each “turn” of the trajectory is associated with statistical weight  $e^{-\epsilon}$  (see Fig. 1). The persistence length in such a case is a function of the bending energy  $l_p \sim e^\epsilon$  (at  $\epsilon > 0$ ). The case where  $\epsilon = 0$  corresponds to the case of a flexible chain ( $l_p = 1$ ). At  $\epsilon \gg 0$ , the bends are energetically unfavorable, which corresponds to the stiff-chain limit ( $l_p \rightarrow \infty$ ). Whereas at  $\epsilon \ll 0$ , the bends become energetically favorable, and very fuzzy “superflexible” chains having a turn associated at each step appear. An interesting example of the physical realization of such a model can be found in biopolymers, where the spatial conformation is mainly determined by the peptide bonds between functional groups. These bonds are responsible for the formation of extended structures such as  $\alpha$ -helices. The break of these bonds under some solvent conditions can lead to the bending and the twisting of a macromolecule, which can be described as the rod-to-coil transition in the frames of our model. Whereas the former limit is deeply related to the “coil-to-rod” transition mentioned before, less is known about the latter case, when a bending is favorable. In particular, the 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  $\epsilon$ , distinguishing the stiff and flexible limits. Applying numerical simulations, we evaluate the explicit bending dependence on the parameter  $\epsilon$  and analyze the properties of the “superflexible” state.

## 2. The Method

To study the conformational properties of self-avoiding random walks on the regular lattice, we use the pruned-

enriched Rosenbluth method [21] combining the original Rosenbluth–Rosenbluth algorithm of growing chains [22] and the control over the growth of a population [23]. 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 the 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 conformation at the  $n$ -th step:

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

where  $m_l$  is the number of free lattice sites to place the  $l$ -th monomer,  $\theta_l$  is an angle between steps  $l$  and  $l - 1$ , and  $\epsilon_l$  is the bending energy at the  $l$ -th step oriented differently than 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 averaging over conformations for any quantity of interest then has the form

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

where the summation is performed over the ensemble of all constructed  $N$ -step SAWs ( $M \sim 10^5$  in our case). Note that, in the literature considering the structurally disordered systems, procedure (4) is usually referred to as the “configurational averaging” [24]. However, since the term “configuration” in polymer physics refers to a fixed sequence of monomers along the chain [3], here and below, we will use the term “conformational averaging” to denote the averaging (4).

The weight fluctuations of the growing chain are suppressed in PERM by pruning the conformations with too small weights, and by enriching the sample with copies of high-weight conformations. These copies are made while the chain is growing and continue to grow independently of one another. 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 conformation is doubled, and the weight

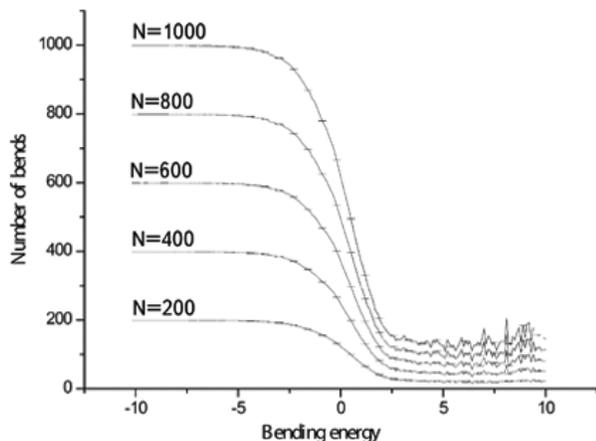


Fig. 2. Number of bends in a polymer chain as a function of the bending energy  $\varepsilon$  at various numbers of monomers  $N$  in  $d = 2$

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 [25, 26]:  $W_n^> = C(Z_n/Z_1)(c_n/c_1)^2$  and  $W_n^< = 0.2W_n^>$ , where  $c_n$  denotes the number of created chains having length  $n$ , and the parameter  $C$  controls the pruning-enrichment statistics; it is adjusted such that 10 chains of the total length  $N$  are generated per each tour on the average [26].

### 3. Results and Discussion

Applying the PERM algorithm, we analyze the conformational properties of semiflexible SAWs under varying the bending energy  $\varepsilon$  in spaces with the 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  $-10, \dots, 10$ .

To describe quantitatively the extent of chain flexibility or stiffness, let us evaluate the number of bends in a polymer chain of length  $N$  corresponding to the number of times when the SAW trajectory changes its direction. Figures 2 and 3 present our simulation results. The case  $\varepsilon = 0$  corresponds to the regime of a flexible polymer coil with averaged size measure given by Eq. (1). For negative values of  $\varepsilon$ , the bends becomes more and more favorable. In the limit  $\varepsilon \ll 0$ , we obtain 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 2D and 3D cases, we can estimate the marginal value of  $\varepsilon \simeq -3.5$ , below which the “superflexible” state

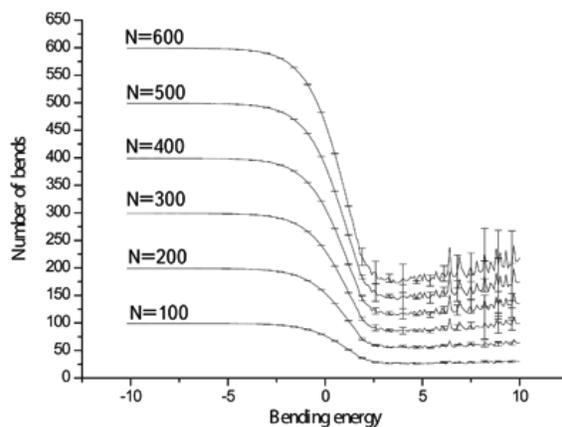


Fig. 3. Number of bends in a polymer chain as a function of the bending energy  $\varepsilon$  at various numbers of monomers  $N$  in  $d = 3$

occurs. For positive  $\varepsilon$ , when each bending of a trajectory leads to the total energy increase, 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 chains,  $N \leq 100$ .

Whereas, in most 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 arises: What is the typical shape of such a conformation? One could expect, in principle, the zigzag conformation, as is shown in the middle of Fig. 4.

We can shed light into this question by studying the averaged number of nearest neighbor contacts  $p$  (i.e., number of cases where two nearest neighbor sites are occupied but not connected by a bond) of a typical polymer chain. It is obvious that, for a completely stretched rod-like conformation, we will have  $p = 0$ , whereas for the expected zigzag-like structure,  $p = 1$  (in  $d = 2$ ), as is sketched in Fig. 4. Our numerical results for  $p$  values as a function of the bending energy  $\varepsilon$  for SAWs in  $d = 2$  are presented in Fig. 5. At  $\varepsilon = 0$  corresponding to the ordinary SAW problem, the value of nearest neighbor contacts in  $d$  dimensions can be estimated from the empirical relation

$$p = 2d - 1 - z(d), \quad (5)$$

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 where the trajectory is allowed to cross itself (so-called random walks), it is easy to show for a (hyper)cubic lattice in  $d$  dimen-

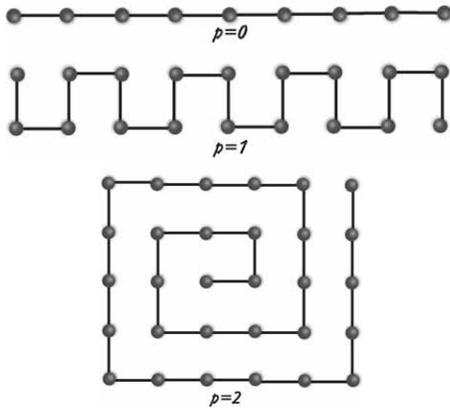


Fig. 4. Schematic presentations of SAW trajectories in  $d = 2$  with the numbers of nearest neighbor contacts  $p = 0$  (rod-like conformation),  $p = 1$  (zigzag conformation), and  $p = 2$  (compact globule)

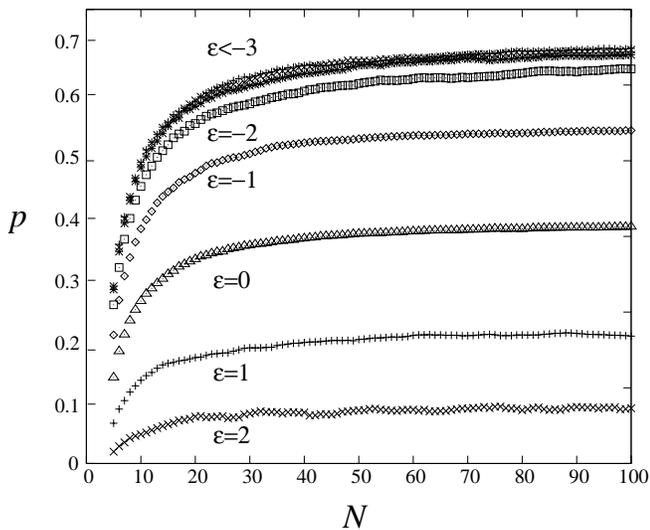


Fig. 5. Number of contacts with nearest neighbors in a SAW trajectory in  $d = 2$  as a function of the chain length  $N$  at various values of bending energy  $\epsilon$

sions that  $z(d) = 2d$ . Taking the self-avoidance effect into account, the “turning back” at each step is forbidden. This reduces the fugacity to the value  $2d - 1$ . Finally, we notice that another factor which reduces the fugacity due to the self-avoidance effect is the contacts with nearest neighbors  $p$ . Substituting the known value  $z(d = 2) = 2.6385 \pm 0.0001$  [27] into (5), we obtain an estimate for the ordinary SAW:  $p = 0.361$ . Our result for the case  $\epsilon = 0$  obtained by the least-square fitting of data gives  $p = 0.354 \pm 0.009$ , which is thus nicely supported. Note, however, that the above quantity is not universal. In particular, it depends on the lattice type.

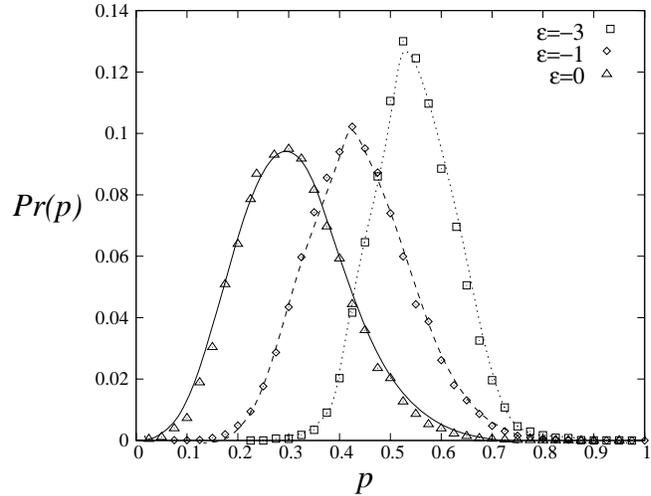


Fig. 6. Probability distribution of the number of nearest neighbor contacts in a  $N = 40$ -step SAW trajectory in  $d = 2$  at various values of bending energy  $\epsilon$

Therefore, the numerical values of  $p$ , strictly speaking, reflect properties of SAWs on a simple cubic lattice and cannot be directly used in the description of polymers in a continuous space (in a good solvent). This is opposite to the universal quantities of polymers (as the scaling exponent  $\nu$  (1)), which are perfectly described by the lattice model of SAW.

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

#### 4. Conclusions

We have studied the conformational properties of semi-flexible polymers within the lattice model of self-avoiding walks with additional bending parameter  $\epsilon$ , which is negative for the “gauche” step preference (step which is not in the same direction as the preceding step) and positive for the “trans” step preference [10, 13, 16, 20]. Typical examples of flexible polymers (with bending energy  $\epsilon = 0$  within this model) are synthetic polymers with a carbon backbone such as polyethylene, where the neighboring carbon atoms can easily rotate around single  $\sigma$ -bonds [1–3]. Under the external influence, these macromolecules can also adopt the superflexible zigzag

conformations (which may correspond to  $\varepsilon < 0$ ). Many organic macromolecules such as DNA and some proteins are characterized by a massive side-groups (e.g., radicals of amino acids) along the carbon backbone, which leads to an increase in the stiffness (these are semiflexible polymers corresponding in our model to the case  $\varepsilon > 0$ ) [8, 9]. Moreover, some synthetic polymers are characterized by the stiffness over short distances along the chain (polystyrene with side phenol groups) [3]. As examples of stiff rod-like molecules ( $\varepsilon \gg 0$ ), one can name the so-called amphiphiles, usually having the form of a hydrophobic carbon chain with polar group on the one end (phospholipids).

An important characteristics of the semiflexible polymers with “trans” step preference is the persistence length  $l_p$ . At scales smaller than  $l_p$ , a polymer attains the limit of a rigid rod. Whereas, on the chain length much larger than the persistent length, any polymer behaves as a flexible chain consisting of independent segments of the size  $l_p$ . Another interesting case is the “gauche” step preference ( $\varepsilon < 0$ ) describing the situation where the bends are favorable, and, in the limit  $\varepsilon \rightarrow -\infty$ , a “superflexible” chain with turning at each step is predicted.

We considered the “coil-to-rod” transition and properties of the “superflexible” state by studying the averaged number of bends in the typical SAW conformation as a function of  $\varepsilon$ . The existence of a marginal value of  $\varepsilon \simeq -3.5$  is obtained, below which the polymer chain consisting of  $N$  monomers has  $N - 1$  bends and thus is in the “superflexible” state. This is also confirmed by studying the averaged nearest contact number  $p$ , which characterizes the topological properties of a polymer conformation. 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  $0.690 \pm 0.009$  at  $\varepsilon \leq -3.5$ .

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КОНФОРМАЦІЙНІ ВЛАСТИВОСТІ НАПІВГНУЧКИХ  
ПОЛІМЕРІВ: ЧИСЛОВІ СИМУЛЯЦІЇ

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Резюме

Досліджено конформаційні властивості напівгнутих полімерів застосовуючи ґраткову модель випадкових блукань без са-

моперетинів (self-avoiding walks – SAW) із енергією згинання  $\epsilon$ , залежною від взаємоорієнтації послідовних кроків. Застосовано алгоритм Розенблюта із збідненням та збагаченням (PERM). Проаналізовано випадки, коли згини енергетично вигідні ( $\epsilon < 0$ ) та невигідні ( $\epsilon > 0$ ), і обговорено деталі переходу “клубок–стержень” та властивості “надгнутого” стану.