Polymers in crowded environment under stretching force: Globule-coil transitions

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We study flexible polymer macromolecules in a crowded (porous) environment, modeling them as selfattracting self-avoiding walks on site-diluted percolative lattices in space dimensions d=2,3. The influence of stretching force on the polymer folding and the properties of globule-coil transitions are analyzed. Applying the pruned-enriched Rosenbluth chain-growth method, we estimate the transition temperature T_{Θ} between collapsed and extended polymer configurations and construct the phase diagrams of the globule-coil coexistence when varying temperature and stretching force. The transition to a completely stretched state, caused by applying force, is discussed as well.

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I. INTRODUCTION

Long flexible polymer macromolecules in a good solvent possess configurational statistics which is perfectly captured by the model of self-avoiding (random) walks (SAWs) on a regular lattice [1]. This corresponds to the *regime of polymer coils* which holds provided that the temperature T is above the so-called Θ temperature. In this regime, the mean endto-end distance of an N-step chain scales as $R_N \sim N^{\nu_{\text{SAW}}}$, where ν_{SAW} is a universal exponent, which depends on space dimension d only $[\nu_{\text{SAW}}(d < 4) > 1/2, \nu_{\text{SAW}}(d \ge 4) = 1/2].$ When lowering the temperature, the effect of monomermonomer attraction grows and the polymer radius shrinks. At $T=T_{\Theta}$ the effective repulsion due to the volume exclusion constraint is exactly balanced by attractive interactions. At this particular temperature a crossover occurs from high temperature SAW behavior to Θ statistics with exponents $\nu_{\Theta}(d$ =2)=4/7 [2], $\nu_{\Theta}(d \ge 3)=1/2$. Below the Θ temperature, the entropic effects, which make the polymer chain swell, are overcome by interaction energy and a collapse to the globule *regime* (with collapsed size exponent $\nu_c = 1/d$) occurs. It is generally accepted [1] that the coil-globule transition is of second order in the sense that the density of an infinite globule is zero at $T=T_{\Theta}$ and increases continuously when T is lowered further; more precisely, it is a tricritical point with the upper critical dimension $d_c=3$.

The coil-globule transition is one of the fundamental problems in polymer physics [1,3,4], being deeply connected with problems such as protein folding, DNA condensation, and chromatin organization. The properties of polymers in the vicinity of the Θ point can be successfully studied on the basis of self-attracting self-avoiding walks (SASAWs), where a nearest-neighbor interaction is included. The coil-globule transition of flexible polymers has been so far the subject of numerous studies [5–13]. Note that the Θ temperature is a nonuniversal quantity, depending on the lattice type; in particular it appears to be proportional to the connectivity

constant μ of a SAW on a given type of lattice (numerical estimates of μ and Θ temperatures on simple square and cubic lattices are compiled in Table I).

The recent progress in experimental techniques employing optical tweezers [14], atomic force microscopy [15], and soft microneedles [16] makes it possible to monitor the behavior of various polymers under tension and stress. In particular, applying a force on an isolated protein, the mechanism of force-driven phase transitions was studied, such as the unfolding of the giant titine protein [17] or the stretching and unzipping of collapsed DNA molecules [18]. Of special interest in biophysics is the stretching of a collapsed polymer, i.e., of a polymer in a poor solvent below the Θ temperature. Unfolding proteins in this way could give important information on their spontaneous folding pathways. An intriguing question is whether intermediate stages observed in different protein denaturating processes under applied force would always correspond to folding pathways in an enforced environment [19-21]. Note that varying temperature alone, a polymer cannot acquire the conformation of the completely stretched state with size exponent $\nu = 1$. Hence force not only influences the elastic, mechanical, and structural properties of polymers but also introduces a new stretched state (regime of string) which is otherwise not accessible. The properties of force-induced globule-coil and coil-string transitions in d=2,3 have been studied intensively both analytically [25-29] and applying numerical simulations [27,30]. The ex-

TABLE I. Values of connectivity constants and Θ temperatures for SASAWs on pure regular lattices and site-diluted percolative lattices for different space dimensions *d*.

d	μ	T_{Θ}	μ_{p_c}	$T^{p_c}_{\Theta}$ (our study)
2	2.6385(1) ^a	1.499(2) ^b	1.565(2) ^c	0.92(2)
3	4.68404(9) ^d	3.717(3) ^e	$1.462(2)^{c}$	0.71(2)

^aReference [22].

^bReference [11].

^cReference [24].

^dReference [23].

^eReference [10].

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istence of many intermediate states was found when unfolding under an applied force, which are not the same as the thermodynamically stable intermediate states. The phase diagrams of the globule-coil and coil-string coexistence when varying temperature and stretching force were constructed.

New challenges have been raised recently in studying protein folding in the natural cellular environment [31]. Real biological cells can be described as a very crowded environment built of various biochemical species, which occupy a large fraction of the total volume; the "volume exclusion" arises due to the steric repulsion between molecules [32]. In the language of lattice models, the crowded environment with structural obstacles can be considered as a disordered lattice, where some amount of randomly chosen sites contains defects. Of particular interest is the case when the concentration p of lattice sites allowed for the SAWs equals the critical concentration p_c ($p_c(d=2)=0.592746$ [33], $p_c(d=2)=0.592746$ $=3)=0.311\ 60\ [34])$ and the lattice becomes percolative. An incipient percolation cluster appears in the system, on which infinitely long SAWs can reside. In this regime, the scaling law for the end-to-end distance holds with a new exponent $\nu_{p_c} > \nu_{\text{SAW}}$ [24,35–41]. A hint to the physical understanding of this phenomenon is given by the fact that the percolation cluster itself is a fractal object with fractal dimension d_p^F dependent on *d*. In this way, scaling law exponents of SAWs change with the dimension $d_{p_c}^F$ of the (fractal) lattice on which the walk resides. Note that studying the scaling of SAWs on a percolative lattice, one is interested rather in the backbone of the percolation cluster, which is defined as follows. Assume that each site of the cluster is a resistor, the neighbor sites are connected by conducting bonds, and an external potential drop is applied at two ends of the cluster. The backbone is the subset of the cluster consisting of all sites through which the current flows; i.e., it is the structure left when all "dangling ends" are eliminated from the cluster. The SAWs can be trapped in dangling ends; therefore infinitely long chains can only exist on the backbone of the cluster, which is characterized by its own fractal dimension $d_{p_c}^B$ ($d_{p_c}^B(d=2)=1.650\pm0.005$ [42], $d_{p_c}^B(d=3)=1.86\pm0.01$ [42]).

Whereas the scaling behavior of SAWs on percolative lattices served as a subject of numerous studies since the early 1980s (see, e.g., Ref. [43] for a review), less attention has been paid to peculiarities of the influence of the fractal structure of the underlying lattice on properties of the coil-globule transition. The upper critical dimension shifts to $d_c=6$ for both SAW and Θ -point statistics on a disordered lattice at the percolation threshold. The scaling of polymer size at the coilglobule transition point is governed by $\nu_{\Theta}^{p_c} > \nu_{\Theta}$ for $d \le 6$ (e.g., $\nu_{\Theta}^{p_c}(d=2)=0.74\pm0.02$ [44], $\nu_{\Theta}^{p_c}(d=3)=0.60\pm0.02$ [44]). It is established that the value of the Θ temperature is lowered due to the presence of disorder [43–49], but estimates for $T^{p_c}_{\Theta}$ were found up to now only for the case of bond percolation. The existing estimates are $T_{\Theta}^{p_c}(d=2)=0.62(6)$ [45], $T_{\Theta}^{p_c}(d=3)=0.43(6)$ [43] (note that the corresponding values of connectivity constants for SAWs on bond-diluted percolative lattices read as $\mu_{p_c} \simeq 1.29$ and 1.05 for d=2 and 3, respectively [43]).

The response of a polymer in crowded media to the stretching force modeled by the SASAW model on percola-

tive lattice has been considered so far only in d=2 for relatively short chains by exact enumeration [50]. However, much more important is studying this problem in three dimensions, which describes real polymer systems. This still needs a careful analysis and clarification. Also, a quantitative description of the globule-coil transition under applied force, in particular the estimate of Θ temperatures in disordered environments under stretching, still remains an open question.

The aim of the present study is to apply state-of-the-art numerical simulations to analyze the properties of SASAWs on site-diluted lattices at the percolation threshold (modeling flexible polymers in a crowded environment) under applied external stretching force in space dimensions d=2,3. We estimate the shift of the Θ temperature of the globule-coil transition under the influence of stretching and analyze the effect of applied force on the phase transitions between collapsed, extended, and stretched phases.

The outline of the rest of the paper is as follows. In Sec. II we describe the details of the numerical algorithm used in our study. In Sec. III we present our results of coil-globule transition peculiarities for SAWs on percolative lattices, and in Sec. IV we analyze the influence of stretching force on properties of the transition between collapsed and extended states. We end up by giving conclusions and an outlook in Sec. V.

II. METHOD

We consider site percolation on regular lattices of edge lengths up to L_{max} =400,200 in dimensions d=2,3, respectively. Each site of the lattice was assigned to be occupied with probability p_c and empty otherwise. To obtain the backbone of a percolation cluster on a given disordered lattice, we apply an algorithm consisting of the following two steps: first finding the percolation cluster based on the site-labeling method of Hoshen and Kopelman [51] and then extracting the backbone of this cluster [52] (the algorithm is explained in detail in our previous papers [41,53]). We constructed 1000 clusters in each space dimension.

To study SASAWs on the backbone of percolation clusters, we apply the pruned-enriched Rosenbluth method (PERM) [10], taking into account that a SASAW can have its steps only on the sites belonging to the backbone of the percolation cluster. PERM is based on the original Rosenbluth-Rosenbluth (RR) method [54] and enrichment strategies [55]. The polymer grows step by step, i.e., the *n*th monomer is placed at a randomly chosen empty neighbor site of the last placed (n-1)th monomer $(n \le N)$, where N is the total length of the chain). The growth is stopped if the total length of the chain is reached. In order to obtain correct statistics, any attempt to place a monomer at an already occupied site would result in discarding the entire chain. This leads to an exponential "attrition" (the number of discarded chains grows exponentially with the chain length). The bias due to avoiding this case is corrected in the RR algorithm by means of giving a weight $W_n \sim \prod_{l=2}^n m_l$ to each sample configuration at the *n*th step, where m_1 is the number of free lattice sites to place the *l*th monomer. This method is particu-



FIG. 1. (Color online) Self-avoiding walks on the backbone of a percolation cluster in d=2 under stretching force *F*.

larly useful for studying Θ polymers since the Rosenbluth weights of the statistically relevant chains approximately cancel against their Boltzmann probability.

Population control in PERM suggests pruning configurations with too small weights and enriching the sample with copies of high-weight configurations [10]. 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 $W_n^{>}$ depending on the estimate of the partition sum of the *n*-monomer chain. If the current weight W_n of an *n*-monomer chain is less than $W_n^{<}$, a random number r=0,1 is chosen; if r=0, the chain is discarded, otherwise it is kept and its weight is doubled. Thus, low-weight chains are pruned with probability 1/2. If W_n exceeds $W_n^{>}$, the configuration is doubled and the weight of each copy is taken as half the original weight. For updating the threshold values we apply similar rules as in [56] and [57]: $W_n^{>} = C(Z_n/Z_1)(c_n/c_1)^{2}$ 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. After a certain number of chains of total length N are produced, the iteration is finished and a new tour starts. We adjust the pruning-enrichment control parameter such that on average ten chains of total length N are generated per each iteration [57] and perform 10^6 iterations.

One end of the chain is subjected to an external force F acting in a chosen direction, say x (see Fig. 1), while the other end (the starting point) is kept fixed. The stretching energy E_s arising due to the applied force for an *n*-step trajectory is given by

$$E_s = -Fx, \tag{1}$$

where $x \equiv x_n - x_0$ denotes the *x* component of the distance from the starting point. The Rosenbluth weight factor W_n is thus taken to be

$$W_n = \prod_{l=2}^n m_l e^{-[(E_l - E_{l-1}) - F(x_l - x_{l-1})]/k_B T},$$
(2)

where E_l denotes the energy of the *l*-step chain $(E_l=z_l\epsilon$ with ϵ being an attractive energy between two nearest neighbors

and z_l being the number of nearest-neighbor contacts for a given chain) and k_B is the Boltzmann constant. In what follows, we will assume units in which $\epsilon = -1$, $k_B = 1$.

When a chain of total length N is constructed, a new one starts from the same starting point until the desired number of chain configurations is obtained. The configurational averaging, e.g., for stretching in x direction, is then given by

$$\langle x \rangle = \frac{\sum_{\text{conf}} W_N^{\text{conf}}(x_N^{\text{conf}} - x_0^{\text{conf}})}{\sum_{\text{conf}} W_N^{\text{conf}}},$$
(3)

where x_0^{conf} and x_N^{conf} denote the *x* coordinates of start and end points, respectively, and W_N^{conf} is the weight of an *N*-monomer chain in a given configuration.

Note that in studying SAWs on disordered lattices, we have to perform two types of averaging: the first average $\langle \cdots \rangle$ is performed over all SAW configurations on a single backbone of a percolation cluster; the second average $\overline{\langle \cdots \rangle}$ is carried out over different realizations of disorder, i.e., over many backbone configurations.

III. $\boldsymbol{\Theta}$ TRANSITION OF SASAW ON PERCOLATIVE LATTICE

Statistical fluctuations of the energy E of a polymer chain, expressed by the behavior of the specific heat C_V , signalize thermodynamic activity in the system, and thus the peak structure of C_V as a function of temperature indicates transitions or crossovers between physically different states. In the case of a polymer system, this corresponds to the transition between globule and coil regimes. C_V can be expressed via energy fluctuations as follows:

$$C_V(T) = \frac{1}{NT^2} (\overline{\langle E^2 \rangle} - \overline{\langle E \rangle^2}).$$
(4)

It is worthwhile first to discuss the behavior of the energy distribution $\operatorname{Prob}(E)$ with varying temperature of the system, as presented in Fig. 2. Since the energy distribution shows one peak only, the transition could be denoted as being second-order-like. The width of the distribution grows with increasing temperature until it has reached its maximum broadening value. This happens in the vicinity of the Θ point. At higher temperatures, the distribution becomes narrower again.

For comparison with available results and testing our methods, we performed also simulations on pure lattices. Figures 3 and 4 show the specific-heat behavior of SASAWs on a pure lattice and the backbone of percolation clusters in d=2,3 for several different chain lengths. Note that the curves of the specific heat show additional shoulders in temperature ranges below the coil-globule transition. In fact, at temperatures below the Θ point, another transition can occur, called crystallization or freezing transition, leading to additional signals in the specific heat. These correspond to a transition to the maximally compact ground states. Recent studies of freezing and collapse of flexible polymers in d=3 can be found in Ref. [13]. Note that the maximum of the specific



FIG. 2. Energy distribution for N=180-step SASAWs in d=2 at different temperatures. Left: pure lattice; T=0.6 (squares), T=1.0 (diamonds), and T=1.5 (triangles). The broadening of the distribution curve emerges close to $T_{\Theta}=1.499\pm0.002$. Right: backbone of percolation clusters; T=0.2 (squares), T=0.4 (diamonds), and T=0.9 (triangles). The broadening of the distribution curve emerges close to $T_{\Theta}^{p}=0.92\pm0.02$.



FIG. 3. Specific heat per monomer as a function of temperature for a SAW in d=2 on a pure lattice (left) and backbone of percolation cluster (right). Squares: N=50, diamonds: N=100, and triangles: N=150.



FIG. 4. Specific heat per monomer as a function of temperature for a SASAW in d=3 on a pure lattice (left) and backbone of percolation cluster (right). Squares: N=40, diamonds: N=80, and triangles: N=120.



FIG. 5. Peak temperatures of the specific heat of a SASAW in d=2 (left) and d=3 (right) at different chain length *N*. Squares: pure lattice; diamonds: backbone of percolation cluster.



FIG. 6. Energy distribution for N=180-step SASAWs in d=2 under a force F acting in the environment. Left: pure lattice at T=0.4: F=0.1 (squares), F=1.0 (diamonds), and F=1.5 (triangles). Right: backbone of percolation cluster at T=0.1: F=0.1 (squares), F=1.0 (diamonds), and F=1.5 (triangles).



FIG. 7. Specific heat per monomer of a SASAW with N=90 steps in d=2 under stretching force F as a function of temperature. Left: pure lattice; right: backbone of percolation cluster. Squares: F=0.2, diamonds: F=0.4, and triangles: F=0.6.



FIG. 8. Specific heat per monomer of a SASAW with N=90 steps in d=3 under stretching force F as a function of temperature. Left: pure lattice; right: backbone of percolation cluster. Squares: F=0.2, diamonds: F=0.4, and triangles: F=0.6.



FIG. 9. Peak temperatures of the specific heat of a SASAW as a function of chain length *N*. Upper row: d=2, left: pure lattice, and right: backbone of percolation cluster. Lower row: d=3, left: pure lattice, and right: backbone of percolation cluster. Squares: F=0, diamonds: F=0.2, triangles: F=0.4, and circles: F=0.6.



FIG. 10. Phase diagrams of the stretching of a SASAW under applied force *F*. Upper row: d=2, left: pure lattice, and right: backbone of percolation cluster. The solid line presents results of exact enumeration [30]. Lower row: d=3, left: pure lattice, and right: backbone of percolation cluster. The filled triangle presents the result in Ref. [27], F=1.5, $T_{\Theta} \approx 2.46$.

heat per monomer grows with *N* for SAWs on a pure lattice, whereas for the case of the backbone of percolation clusters it decreases with increasing *N*. For finite chain length *N*, the temperature defined by the position of the specific-heat maximum $T_{C_V}^{\max}(N)$ is well below the collapse transition Θ temperature. This finite-size deviation of $T_{C_V}^{\max}(N)$ from T_{Θ} obeys scaling behavior with *N*. Figure 5 presents the chainlength dependence of the specific-heat peaks for pure and percolative lattices. For the case of a pure lattice, *d*=3 is the upper critical dimension for the Θ transition, and the meanfield Flory-Huggins theory [58] suggests

$$T_{C_V}^{\max}(N) - T_{\Theta} \sim \frac{1}{\sqrt{N}} + \frac{1}{2N}.$$
(5)

In the general case, the approach of $T_{C_V}^{\max}(N)$ to its limiting value obeys

$$T_{C_V}^{\max}(N) - T_{\Theta} \sim aN^{-\nu_{\Theta}} + \frac{b}{N},\tag{6}$$

where a, b are constants and ν_{Θ} is the size exponent of a SAW at the Θ point,

d = 2, pure lattice: $\nu_{\Theta} = 4/7$ (Ref. [2]), (7)

$$d = 2$$
, pc: $\nu_{\Theta}^{p_c} = 0.74 \pm 0.02$ (Ref. [44]), (8)

d = 3, pc: $\nu_{\Theta}^{p_c} = 0.60 \pm 0.02$ (Ref. [44]). (9)

Note that we consider the special case of the collapse transition on site-diluted percolative lattices, which was not studied before.

Our estimates for $T_{\Theta}^{p_c}$ are obtained by least-squares fitting of Eq. (6), taking into account Eqs. (8) and (9), and presented in Table I. As it was already mentioned, the collapse transition temperature is a nonuniversal property, which depends on the lattice type and, in particular, on the connectivity constant. As expected, the values of $T_{\Theta}^{p_c}$ appear to be smaller than the pure lattice values as far as the relation $\mu_{p_c} < \mu$ holds. In addition, due to the fact that μ_{p_c} decreases with *d*, the same tendency is reflected in the transition temperature behavior: $T_{\Theta}^{p_c}(d=2) > T_{\Theta}^{p_c}(d=3)$. This is in contrast to the values on the pure lattice but coincides with the tendency of bond-diluted percolation values cited in Sec. I. Let us note, finally, that our values for $T_{\Theta}^{p_c}$ of site percolation are larger than those of bond percolation, which can be explained again

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F	0	0.2	0.4	0.6	0.8	1.0
$T^{p_c}_{\Theta}(d=2)$	0.92(2)	0.84(2)	0.74(3)	0.56(2)	0.40(4)	0.18(5)
$T^{p_c}_{\Theta}(d=3)$	0.71(2)	0.66(2)	0.60(2)	0.48(3)	0.35(2)	0.20(2)

TABLE II. Values of the Θ temperature on the backbone of percolation clusters in d=2,3 at varying force F.

by the difference of the connectivity constants of these two fractal lattice structures.

IV. Θ TRANSITION OF SASAW ON PERCOLATIVE LATTICE UNDER STRETCHING FORCE

Let an additional stretching force F now act in the x direction of a SASAW trajectory, fixed at its starting point (see Fig. 1). The energy distributions Prob(E) at fixed temperature and varying F are presented in Fig. 6 for the cases of the

pure lattice and the backbone of percolation clusters for comparison. We have chosen the value of *T* in both cases to be well below the corresponding Θ temperatures, so that at *F* =0 we restore the energy distribution of the globular state. With increasing *F*, the averaged energy of the chain decreases—applied force stretches the polymer globule. The width of the distribution changes at increasing *F* and reaches its maximum broadening in the vicinity of the Θ point. The value of the transition temperature is now shifted by the presence of force. At higher values of *F*, the distribution



FIG. 11. Averaged extensions of a SASAW under applied force. Upper row: d=2, left: pure lattice (T=0.2), and right: backbone of percolation cluster (T=0.2). Lower row: d=3, left: pure lattice (T=1.8), and right: backbone of percolation cluster (T=0.4). Squares: N = 20, diamonds: N=50, and triangles: N=100.

becomes narrower again-the chain is in an extended state.

To study the Θ transition of SASAWs, when the external stretching force is acting in the environment, we are working in the "constant-force" ensemble. Fixing the value of *F*, we study the specific-heat behavior (Figs. 7 and 8). Analyzing the peak structure of the specific heat, we immediately conclude that increasing the value of *F* leads to decreasing the transition temperature. Figure 9 presents the chain-length dependence of the specific-heat peaks for the pure and percolative lattices at several different values of *F*.

For finite chain length N, the temperature defined by the position of the specific-heat maximum $T_{C_V}^{max}(N)$ is well below the collapse transition Θ temperature. Our estimates for $T_{\Theta}^{p_c}$ in the presence of force are obtained by least-squares fitting of Eq. (6) with Eqs. (7)–(9). Results are presented in Fig. 10 in the form of a phase diagram of transitions from globule to extended state and listed in Table II. For the pure lattice in d=2, we compare our results with an exact enumeration study of Kumar *et al.* [30], where SASAWs of length up to N=55 under stretching force were studied. Our results also appear to be in good correspondence with that in Ref. [27].

The averaged extension in x direction, giving information about the internal structure of the polymer configuration under applied force, is presented in Fig. 11 for the cases of a pure lattice and the backbone of percolation clusters. At small forces, a polymer chain is still in the compact folded state and slightly oriented along the force direction. At larger forces, the polymer chain has a conformation similar to the extended (swollen) structure. Note that completely stretched states, corresponding to $\langle x \rangle / N \approx 1$, can be obtained only in the pure case and are not accessible on the percolative lattices due to the complicated fractal structure of the underlying percolation cluster. Our estimates of $\langle x \rangle / N$ in d=2 appear to be in a good correspondence with that of available exact enumeration studies [30,50].

V. CONCLUSIONS

We studied the self-attracting self-avoiding walks on disordered lattices in space dimensions d=2,3, modeling flexible polymer macromolecules in porous environment. We considered the special case when the concentration of disorder is exactly at the percolation threshold, so that an incipient percolation cluster of sites, allowed for SAWs, emerges on the lattice. In our study, SASAWs reside only on the backbone of the percolation cluster, which has a fractal structure.

In the first part of our study, attention has been paid to the influence of the fractal structure of the underlying lattice on properties of the coil-globule transition. Applying the pruned-enriched Rosenbluth algorithm (PERM), we obtain estimates of the collapse transition temperature $T_{\Theta}^{p_c}$ of SASAWs on site-diluted percolative lattices in d=2 and 3 dimensions (note that so far only estimates for the bond-percolation case have been found). The values of $T_{\Theta}^{p_c}$ appear to be smaller than the pure lattice values. This can be explained, remembering that the collapse transition temperature is proportional to the connectivity constant μ of SAWs on a given lattice. In addition, due to the fact that μ_{p_c} decreases with *d*, the same tendency is reflected in the anomalous transition temperature behavior: $T_{\Theta}^{p_c}(d=2) > T_{\Theta}^{p_c}(d=3)$.

Next, keeping one end of a SASAW trajectory on the backbone of a percolation cluster fixed, we applied a stretching force, acting in some chosen direction (say, *x*). Especially interesting was to study this problem in d=3, which corresponds to real polymer systems and was not considered before. We estimated the shift of the Θ temperature of the globule-coil transition under the stretching and constructed phase diagrams of collapsed and extended states coexistence in d=2,3. As expected, the presence of stretching force in environment leads to a decreasing Θ -temperature value.

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- J. des Cloizeaux and G. Jannink, *Polymers in Solution* (Clarendon Press, Oxford, 1990); P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- [2] B. Duplantier and H. Saleur, Phys. Rev. Lett. 59, 539 (1987).
- [3] A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (American Institute of Physics, New York, 1994).
- [4] C. Vanderzande, *Lattice Models of Polymers* (Cambridge University Press, Cambridge, 1998).
- [5] V. Privman, J. Phys. A 19, 3287 (1986); V. Privman and D. A. Kurtze, Macromolecules 19, 2377 (1986); H. Meirovitch and H. A. Lim, J. Chem. Phys. 91, 2544 (1989).
- [6] R. M. Lam, J. Phys. A 23, L831 (1990).
- [7] D. P. Foster, E. Orlandini, and M. C. Tesi, J. Phys. A 25, L1211 (1992).

- [8] I. Szleifer, E. M. O'Toole, and Z. Panagiotopoulos, J. Chem. Phys. 97, 6802 (1992).
- [9] P. Grassberger and R. Hegger, J. Chem. Phys. **102**, 6881 (1995).
- [10] P. Grassberger, Phys. Rev. E 56, 3682 (1997).
- [11] G. T. Barkema, U. Bastolla, and P. Grassberger, J. Stat. Phys. 90, 1311 (1998).
- [12] R. Brak, P. P. Nidras, and A. L. Owczarek, J. Stat. Phys. 91, 75 (1998).
- [13] T. Vogel, M. Bachmann, and W. Janke, Phys. Rev. E 76, 061803 (2007).
- [14] U. Bockelmann, P. Thomen, B. Essevaz-Roulet, V. Viasnoff, and F. Heslot, Biophys. J. 82, 1537 (2002).
- [15] M. Rief, H. Clausen-Schaumann, and H. E. Gaub, Nat. Struct. Biol. 6, 346 (1999).
- [16] A. Kishino and T. Yanagida, Nature (London) 334, 74 (1988).

- [17] M. Rief, M. Gautel, F. Oesterhelt, J. M. Fernandez, and H. E. Gaub, Science 276, 1109 (1997); M. S. Z. Kellermayer, S. B. Smith, H. L. Granzier, and C. Bustamante, *ibid.* 276, 1112 (1997); L. Tskhovrebova, J. Trinick, J. A. Sleep, and R. M. Simmons, Nature (London) 387, 308 (1997).
- [18] C. G. Baumann, V. Bloomfield, S. B. Smith, C. Bustamante, M. Wang, and S. M. Block, Biophys. J. 78, 1965 (2000); C. Danilowicz, Y. Kafri, R. S. Conroy, V. W. Coljee, J. Weeks, and M. Prentiss, Phys. Rev. Lett. 93, 078101 (2004).
- [19] H. Lu, B. Isralewitz, A. Krammer, V. Vogel, and K. Schulten, Biophys. J. 75, 662 (1998); H. Lu and K. Schulten, Chem. Phys. 247, 141 (1999); Biophys. J. 79, 51 (2000).
- [20] Z. Bryant, V. S. Pande, and D. S. Rokhhsar, Biophys. J. 78, 584 (2000).
- [21] A. S. Lemak, J. R. Lepock, and J. Z. Y. Chen, Phys. Rev. E 67, 031910 (2003).
- [22] A. J. Guttmann and J. Wang, J. Phys. A 24, 3107 (1991).
- [23] D. MacDonald, S. Joseph, D. L. Hunter, L. L. Moseley, N. Jan, and A. J. Guttmann, J. Phys. A 33, 5973 (2000).
- [24] A. Ordemann, M. Porto, H. E. Roman, S. Havlin, and A. Bunde, Phys. Rev. E 61, 6858 (2000).
- [25] A. Halperin and E. B. Zhulina, Europhys. Lett. 15, 417 (1991); Macromolecules 24, 5393 (1991).
- [26] D. Göritz, S. Kreitmeier, and M. Wittkop, J. Macromol. Sci., Phys. **35**, 615 (1996); M. Wittkop, S. Kreitmeier, and D. Göritz, Phys. Rev. E **53**, 838 (1996); S. Kreitmeier, M. Wittkop, and D. Göritz, *ibid.* **59**, 1982 (1999).
- [27] P. Grassberger and H.-P. Hsu, Phys. Rev. E 65, 031807 (2002).
- [28] D. Marenduzzo, A. Maritan, and F. Seno, J. Phys. A 35, L233 (2002); D. Marenduzzo, S. M. Bhattacharjee, A. Maritan, E. Orlandini, and F. Seno, Phys. Rev. Lett. 88, 028102 (2001); D. Marenduzzo, A. Maritan, A. Rosa, and F. Seno, *ibid.* 90, 088301 (2003).
- [29] M. Cieplak, T. X. Hoang, and M. O. Robbins, Phys. Rev. E 70, 011917 (2004).
- [30] S. Kumar, D. Giri, and S. M. Bhattacharjee, Phys. Rev. E 71, 051804 (2005); S. Kumar and D. Giri, *ibid.* 72, 052901 (2005); H. Zhou, J. Zhou, Z. C. Ou-Yang, and S. Kumar, Phys. Rev. Lett. 97, 158302 (2006); S. Kumar and D. Giri, *ibid.* 98, 048101 (2007); S. Kumar, I. Jensen, J. L. Jacobsen, and A. J. Guttmann, *ibid.* 98, 128101 (2007).
- [31] D. S. Goodsell, Trends Biochem. Sci. 16, 203 (1991); A. Horwich, Nature (London) 431, 520 (2004).

- [32] A. Minton, J. Biol. Chem. 276, 10577 (2001).
- [33] R. M. Ziff, Phys. Rev. Lett. 72, 1942 (1994).
- [34] P. Grassberger, J. Phys. A 25, 5867 (1992).
- [35] K. Y. Woo and S. B. Lee, Phys. Rev. A 44, 999 (1991); S. B. Lee, J. Korean Phys. Soc. 29, 1 (1996); H. Nakanishi and S. B. Lee, J. Phys. A 24, 1355 (1991).
- [36] P. Grassberger, J. Phys. A 26, 1023 (1993).
- [37] S. B. Lee and H. Nakanishi, Phys. Rev. Lett. 61, 2022 (1988).
- [38] M. D. Rintoul, J. Moon, and H. Nakanishi, Phys. Rev. E 49, 2790 (1994).
- [39] C. von Ferber, V. Blavatska, R. Folk, and Yu. Holovatch, Phys. Rev. E 70, 035104(R) (2004).
- [40] H.-K. Janssen and O. Stenull, Phys. Rev. E 75, 020801(R) (2007).
- [41] V. Blavatska and W. Janke, EPL 82, 66006 (2008); Phys. Rev. Lett. 101, 125701 (2008).
- [42] C. Moukarzel, Int. J. Mod. Phys. C 9, 887 (1998).
- [43] K. Barat and B. K. Chakrabarti, Phys. Rep. 258, 377 (1995).
- [44] K. Barat, S. N. Karmakar, and B. K. Chakrabarti, J. Phys. I 3, 2007 (1993); J. Phys. A 25, 2745 (1992).
- [45] K. Barat, S. N. Karmakar, and B. K. Chakrabarti, J. Phys. A 24, 851 (1991).
- [46] A. K. Roy and B. K. Chakrabarti, J. Phys. A 20, 215 (1987).
- [47] I. Chang and A. Aharony, J. Phys. I 1, 313 (1991).
- [48] B. K. Chakrabarti and S. M. Bhattacharjee, J. Stat. Phys. 58, 383 (1990).
- [49] S. Bhattacharya and B. K. Chakrabarti, Z. Phys. B: Condens. Matter 57, 151 (1984).
- [50] A. R. Singh, D. Giri, and S. Kumar, Phys. Rev. E 79, 051801 (2009).
- [51] J. Hoshen and R. Kopelman, Phys. Rev. B 14, 3438 (1976).
- [52] M. Porto, A. Bunde, S. Havlin, and H. E. Roman, Phys. Rev. E 56, 1667 (1997).
- [53] V. Blavatska and W. Janke, J. Phys. A 42, 015001 (2009).
- [54] M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. 23, 356 (1955).
- [55] F. T. Wall and J. J. Erpenbeck, J. Chem. Phys. 30, 634 (1959).
- [56] H. -P. Hsu, V. Mehra, W. Nadler, and P. Grassberger, J. Chem. Phys. **118**, 444 (2003).
- [57] M. Bachmann and W. Janke, Phys. Rev. Lett. 91, 208105 (2003); J. Chem. Phys. 120, 6779 (2004).
- [58] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).