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Monte Carlo Computer Simulation of a Single Semi-Flexible Macromolecule at a Plane Surface

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Summary: The properties of a single semiflexible mushroom chain at a plane surface with a long-ranged attracting potential are studied by means of lattice Monte Carlo computer simulation using the bond fluctuation model, configurational bias algorithm for chain re-growing and the Wang-Landau sampling technique. We present the diagram of states in variables temperature T vs. strength of the adsorption potential, ε_w, for a quite short semiflexible chain consisting of $N = 64$ monomer units. The diagram of states consists of the regions of a coil, liquid globule, solid isotropic globule, adsorbed coil and cylinder-like liquid-crystalline globule. At low values of the adsorption strength ε_w the coil–globule and the subsequent liquid–solid globule transitions are observed upon decreasing temperature below the adsorption transition point. At high values of ε_w these two transitions change into a single transition from an adsorbed coil to a cylinder-like liquid-crystalline solid globule. We conclude that for a semiflexible chain the presence of a plane attracting surface favors the formation of a globule with internal liquid-crystalline ordering of bonds.

Keywords: adsorption; Monte Carlo computer simulation; semi-flexible macromolecule

Introduction

Polymer adsorption on substrates is an exiting problem of statistical thermodynamics.[1–10] The general problem of an adsorption of a flexible chain from a dilute solution (good or θ-solvent) on a flat non-structured substrate has been studied theoretically already more than 50 years ago.[11] Since that time this problem has been studied by many different theoretical methods (scaling,[12] renormalization group theory[3,13,14]) as well as by computer simulations.[13,15–25] Nevertheless, there are still many open questions.[10] Namely, the question about the influence of stiffness variance on the thermodynamics of the adsorption transition from a three-dimensional coil conformation to a two-dimensional "pancake" conformation[12–16] has not been investigated systematically; semiflexible polymers at surfaces have been studied only occasionally and in other contexts.[26–30]

The problem of adsorption of semiflexible polymers at a plane surface is very interesting due to many reasons. First of all, it is natural to expect that the influence of the chain stiffness on the interaction between biopolymers and biomembranes is quite strong because the biopolymers are usually stiff-chain macromolecules. Moreover, real experiments[31] are very often performed on chains adsorbed on a substrate (AFM studies).

The diagram of states (obtained by theory and computer simulations) for a single semiflexible chain in bulk shows up the regions of stability of toroidal structure as well as other globular structures where a local short-range nematic ordering of segments takes place.[32–40] Taking into account the existence of toroidal globular state for DNA molecules both in the bulk and at a surface, the question whether these toroidal structures are stabilized at the wall is very important and needs additional study.

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Upon increasing the solvent density there is an interesting interplay between phase separation and nematic ordering;[41] the theoretical description of these phenomena is non-trivial because of the strong coupling between nematic fluctuations and structural properties of a single chain;[42] computer simulation study is possible at quite low stiffness values[43] where no nematic ordering occurs, while they are very difficult for more stiff-chain polymers.[44]

In the present paper we study the diagram of states for a single semiflexible chain of the length $N = 64$ monomer units at an attracting surface. We are mainly interested in investigating the changes in structural properties in the vicinity of an adsorbing surface in comparison to a bulk, i.e. whether some new structures appear and how the already existing structures are changed. Our goal is to understand the interplay between the adsorption transition and the coil–globule and liquid–solid globule transitions, with possible formation of intraglobular orientational ordering (isotropic— nematic transition) as well as layering (crystallization) at a surface.

Model and Simulation Technique

We use here the well known bond fluctuation model[45–47] for a single self-avoiding chain on the simple cubic lattice. Each monomer unit occupies 8 lattice sites. The set of bond vectors ensures that the bonds do not cross each other in the course of their local moves. We consider in the present manuscript the case of a single mushroom chain, i.e. the first monomer unit of this chain is anchored to an attracting surface at $z = 0$. We used in our simulation only a chain consisting of $N = 64$ monomer units, and we have chosen the anchoring point at the position $(x,y,z) = (40,40,0)$ in the simulation box of the size $L_x = L_y = 80$, $L_z = 150$. Periodic boundary conditions were applied along x and y axes while hard impenetrable walls were placed at $z = 0$ and $z = L_z$. The box size along z axis, L_z, was chosen to be large enough to ensure a chain totally elongated in this direction being unperturbed.

Bending potential and attracting intermonomer contact interaction potential are taken in the form[36]

$$U_{contact}(r) = \begin{cases} -\varepsilon, & r = 2, \sqrt{5}, \sqrt{6}, \\ 0, & \text{otherwise.} \end{cases} \qquad (1)$$

$$U_{bending}(\vartheta_i) = \varepsilon_\alpha(1 - cos\vartheta_i), \qquad (2)$$

where ϑ_i is the angle between the successive bond vectors $\vec{l_i}$ and $\vec{l}_{i+1}$, ε and ε_α are the energetic parameters measured in the units of k_BT.

To model the adsorption transition we applied the surface potential in the form:

$$U_{adsorption}(z) = \begin{cases} -\dfrac{4\varepsilon_w}{z^3}, & z \geq 2; \\ -\varepsilon_w, & z = 0, 1. \end{cases} \qquad (3)$$

where z is the distance from the wall, i.e. the attracting wall is placed at $z = 0$, while the purely repulsive one is located at $z = L_z$. Monomer units having their origin at $z = 0$ or at $z = 1$ have the lowest wall interaction energy. We have chosen the long–range attracting part of the adsorption potential to be of the same form as that used in Ref. 10. This potential can be justified as the result of integrating a standard Lennard-Jones potential between monomer units and individual wall atoms over a three-dimensional half-space.

We fix the parameter of the intermonomer attracting interaction $\varepsilon = 1$. We consider the temperature T as the parameter to control the coil-globule transition, and the energy of attraction of a single monomer unit to the surface, ε_w, as the parameter controlling the adsorption transition. The stiffness is controlled by the parameter ε_α. In the present study we have used only a single value for this parameter, $\varepsilon_\alpha = 4$, which corresponds to a moderate stiffness.

The properties of this model in the bulk are well know from many previous studies. The knowledge of the coil— globule transition temperature[36,48–50] and its dependence on stiffness,[33–36] the liquid— solid globule transition point[36,48,50] and its dependence on stiffness,[36] as well as parameters for isotropic— nematic transition in semidilute solution[44] helped us to make an appropriate choice of the values of parameters for our simulation.

To change the conformation of the mushroom chain we used the local moves of monomer units as well as configurational bias (CB) algorithm.[51,52] Additionally, we have implemented the Wang-Landau (WL) sampling technique[53,54] to get the flat histogram for the total energy E. Local moves and CB moves used in combination with WL algorithm allow to obtain reasonably good estimates for the density of states $g(E)$.

The acceptance probability for local move was chosen according to WL algorithm:

$$accept = min\{1, g(E_{old})/g(E_{new})\}, \tag{4}$$

where E_{old} and E_{new} are the total energies of the old and the new conformations, respectively.

For CB moves we have used the following procedure. We chose a monomer unit i^* inside the mushroom chain at random and remove the part of the chain between this monomer unit and the free end of the chain starting from the free end monomer and calculating the number $k_i^{(old)}$ of free (not occupied) lattice sites where the particular removable monomer unit i could potentially have its position. Then, we re-grow the removed part of the chain in a new conformation choosing the position of the next monomer unit i at random out of $k_i^{(new)}$ possible non-occupied lattice sites. Afterwards we calculate the weights of the old and the new conformations

$$w_{new} = \prod_{i=i*+1}^{N} k_i^{(new)}, \qquad w_{old} = \prod_{i=N}^{i*+1} k_i^{(old)}; \tag{5}$$

and finally accept this trial move with the probability

$$accept = min\{1, g(E_{old})/g(E_{new}) \cdot w_{new}/w_{old}\}. \tag{6}$$

We divide the whole interval of the total energy, E, in sub-intervals (windows) of the width about $200k_BT$. We start simulation in each window with $g(E) \equiv 1$ for all values of E. We accumulate the histogram of E and simultaneously update the density of states $g(E)$ until the histogram of E becomes flat within the pre-defined deviation width (error bar), which is the so called flatness parameter. The length of such an iteration of the WL algorithm is not fixed. Then, we update the f factor and the flatness parameter (we start from the flatness parameter equal to 0.2 and then multiply it by 0.95 after every iteration of the WL algorithm) and put the histogram of energy to zero. The total number of MC steps used for one simulation run for given value of parameter ε_w was about $5 \cdot 10^8$. The iteration procedure for calculation of $g(E)$ converged approximately after $3 \cdot 10^8$ MC steps. We used about 10^4 Monte Carlo steps (MCS) between every two measurements of observable parameters. Averaging was performed using about 10^4 last measurements, it means that for every value of energy we have sampled about 50–75 conformations. Afterwards, we have combined all windows in the whole interval of the total energy. In particular, for values $\varepsilon_w = 0$, 0.5 and 1 we have used a single interval for E and sampled the statistics over 14–17 thousands conformations, while for $\varepsilon_w = 6$ we divided the whole energy range in 3 sub-intervals and sampled about 70 thousands conformations.

Density of states $g(E)$ was used to calculate the temperature dependencies of observable parameters, i.e. the gyration radius, the total energy and different energy terms, parameters of the globular shape and intraglobular orientational ordering of segments, etc., as well as their histograms in the wide region of T using the following re-weighting formulas:

$$\langle E\rangle(T) = \frac{1}{Z(T)} \sum_E E g(E) e^{-E/k_BT}; \qquad Z(T) = \sum_E g(E) exp\left(-\frac{E}{k_BT}\right) \tag{7}$$

$$\langle R_G^2\rangle(T) = \frac{1}{Z(T)} \sum_E \overline{R}_G^2(E) g(E) e^{-E/k_BT}, \quad \text{where} \quad \overline{R}_G^2(E) = \frac{\sum_{conf,E} R_G^2}{\sum_{conf,E} 1} \tag{8}$$

In the formula for gyration radius, Equation (8), the averaging over conformations with given value of the total energy E is performed using the multiple histogram file accumulated in the course of simulation run.

Shape parameters K_1 and K_2

$$K_1 = \frac{\langle L_2 \rangle + \langle L_3 \rangle}{\langle L_1 \rangle + \langle L_2 \rangle}, \quad K_2 = \frac{\langle L_1 \rangle + \langle L_3 \rangle}{\langle L_1 \rangle + \langle L_2 \rangle}, \tag{9}$$

where L_1, L_2, L_3 are the three principal moments of the gyration tensor, characterize the overall shape of a chain conformation.[55] The values $K_1 = K_2 = 1$ correspond to a perfect sphere, while an infinitely thin rod has the values $K_1 = 0$, $K_2 = 1$, and an infinitely thin disk $K_1 = K_2 = 1/2$ (see also Refs.[34–36]).

The intraglobular orientational ordering of bond vectors can be characterized by orientational order parameters which are the eigenvalues η_1, η_2, η_3 of the tensor

$$Q_{\alpha\beta} = \frac{1}{N-1} \sum_{i=1}^{N-1} \frac{1}{2} \left(3 \left\langle e_i^{\alpha} e_i^{\beta} \right\rangle - \delta_{\alpha\beta} \right), \tag{10}$$

where $ei\alpha$ is the α-th component of the unit vector $\vec{e}_i \equiv \vec{l}_i / |\vec{l}_i|$ along the bond $\vec{l}_i$ connecting monomers i and $i+1$.

Diagram of States for a Single Semiflexible Mushroom Chain at an Adsorbing Surface

In the Figure 1 the diagram of states in variables T—ε_w for a single mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at an attracting surface is shown. It contains the regions of coil (I), liquid globule (II), solid globule (III), adsorbed quasi-two-dimensional coil (IV), and two-dimensional cylinder-like globule (V), which is actually both a crystalline and a liquid-crystalline globule because of the presence of both the translational and orientational ordering of monomer units and bond vectors, respectively.

Let us now discuss in detail how the transition lines (points) have been determined. The temperature dependence of the total energy (Figure 2) shows up a broad and smooth adsorption transition followed by a sharp collapse (coil–globule) transition upon decreasing temperature. For small values of ε_w there is also a subsequent liquid–solid transition which is even more sharp and quite close to the coil–globule transition for this quite short chain length (cf. Refs.[36,48]). This liquid–solid transitions is hardly visible in Figure 2, but it can be much better seen on the temperature dependencies of the contact energy (not shown here) or its derivative (Figure 3).

At low values of adsorption strength $\varepsilon_w = 0$, 0.5 and 1 the derivative of the contact energy (Figure 3) shows up two maxima indicating the coil–globule (at higher temperature) and the liquid–solid transitions. Actually, the two peaks almost overlap, and the smaller peak for the coil–globule transition is visible as a wing on the right side of the large maximum. This is in agreement with the results for these two transitions obtained for a free chain of the length $N = 64$ (cf. Ref.[36,48] where both transitions were found to be quite close to each other both for a flexible and semiflexible chain).

For larger values of ε_w the maximum corresponding to the coil–globule transition merges with that one for the liquid–solid transition, and we observe only one transition, but this transition is actually between an adsorbed coil and a cylinder-like (liquid)-crystalline globule, i.e., this is a coil–solid or coil–crystal transition (see data and discussion below).

The temperature dependence of the adsorption energy (Figure 4) also shows up a two step process: first, there is a very smooth decrease of energy in the course of adsorption transition, and then there is an increase of this energy due to the collapse transition because monomer units loose contacts with the wall when a three-dimensional globule is formed. Adsorption transition temperature increases upon increasing ε_w. This can be understood very well taking into account that adsorption to a wall is not so drastic from the point of

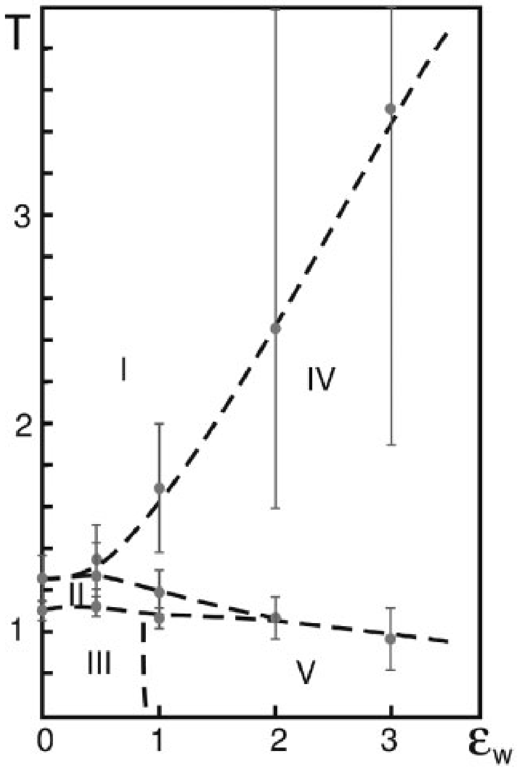


Figure 1.
Diagram of states, T vs. ε_w, for a single semiflexible ($\varepsilon_\alpha = 4$) mushroom chain consisting of $N = 64$ monomer units: I–coil; II–liquid globule; III–solid globule; IV–adsorbed coil; V–two-dimensional cylinder-like globule. Points indicate the positions of maxima on the derivatives of temperature dependencies of the contact energy and the adsorption energy for the coil-globule and the adsorption transition, respectively. Error bars indicate the width of a particular maximum.

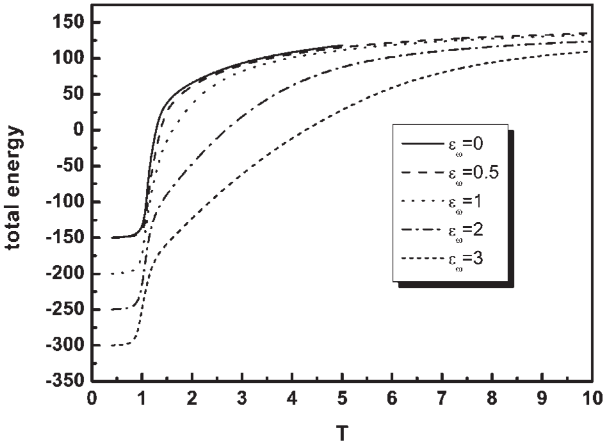


Figure 2.
Temperature dependence of the total energy for a semiflexible mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at an adsorbing wall for different values of adsorption parameter ε_w as indicated in the legend.

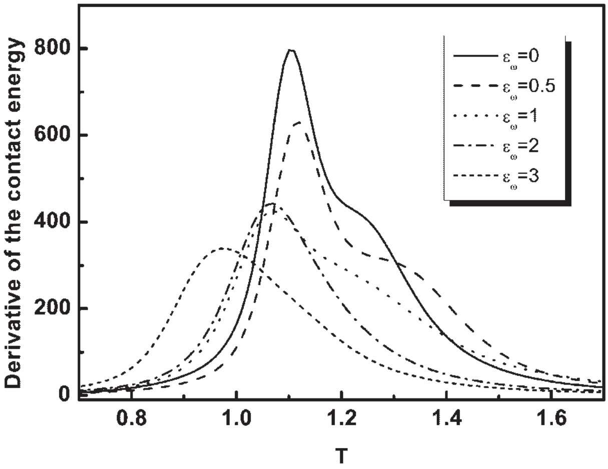


Figure 3.
Temperature dependence of the derivative of the contact energy for a semiflexible mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at an adsorbing wall for different values of adsorption parameter ε_w as indicated in the legend.

view of loosing the entropy in comparison to the collapse transition. For high values of adsorption parameter $\varepsilon_w \sim 6$ there is no desorption from the wall upon decreasing T. This indicates that the solid (liquid)-crystalline globules are almost perfectly two-dimensional at high adsorption strength.

The adsorption transition line in the phase diagram (Figure 1) was determined from the maximum of the derivative of the adsorption energy, while the coil–globule and liquid–solid globule transitions were determined from the maxima on the derivatives of the temperature dependencies of the contact energy, mean squared gyration radius and its projections on the coordinate axes, as well as from the histograms of the number of contacts per one monomer unit.

Let us now look at the temperature dependencies of the components of the mean squared gyration radius in the directions parallel and perpendicular to the wall,

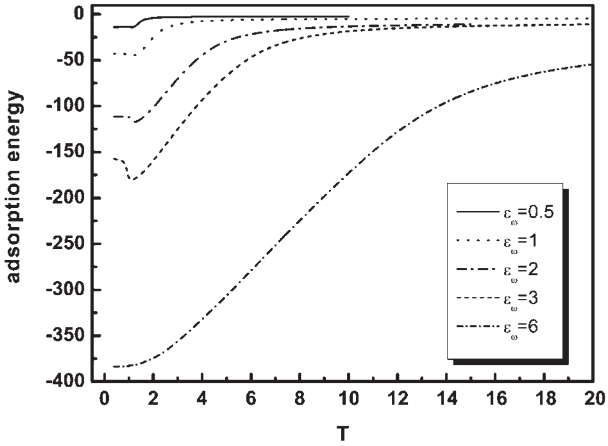


Figure 4.
Temperature dependence of the adsorption energy for a semiflexible mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at an adsorbing wall for different values of adsorption parameter ε_w as indicated in the legend.

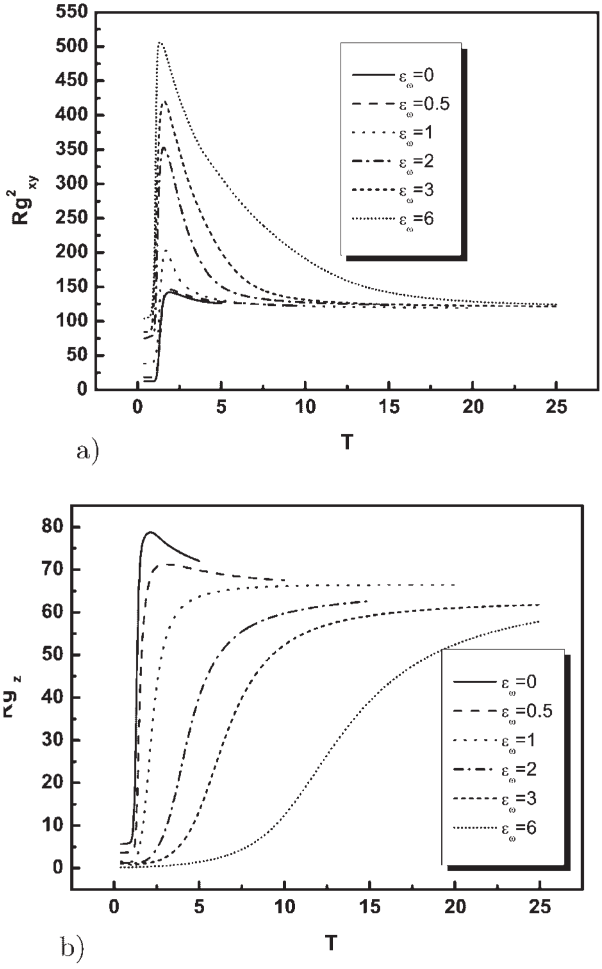


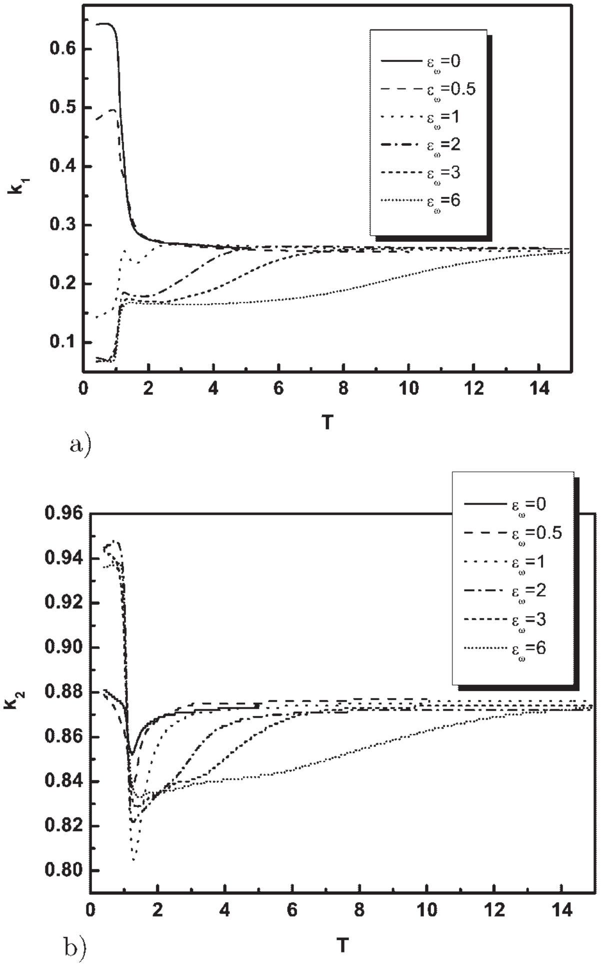
Figure 5.

Temperature dependence of the *xy*- (a) and *z*-components (b) of the squared gyration radius for a semiflexible mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at an adsorbing wall for different values of adsorption parameter ε_w as indicated in the legend.

$R^2_{g,xy}$ and $R^2_{g,z}$, respectively (Figure 5). For the small values of adsorption strength, $\varepsilon_w = 0$ and 0.5, the coil–globule transition is accompanied by a moderate pre-transitional swelling which is uniform in all directions, i.e. the increase of $R^2_{g,z}$ is comparable with that of $R^2_{g,xy}$. This is a pure effect of the stiffening of the chain upon decreasing temperature because of our choice of the bending potential.

Then, upon increasing ε_w we observe a very pronounced spreading of the mushroom over the surface because of the adsorption transition, which shadows the pre-transitional swelling effect due to the chain stiffness. For $\varepsilon_w \geq 1$ the z-component of the squared gyration radius decreases monotonically with decreasing T and reaches a plateau at very low temperatures, while the value of this plateau decreases with increasing ε_w. The xy-component of gyration radius shows up a very pronounced increasing upon decreasing T due to the adsorption, but then a very abrupt collapse transition takes place (this is the transition between the states of an adsorbed coil and a cylinder-like liquid-crystalline globule as we will see later). At very low temperatures $R^2_{g,xy}$ also reaches a plateau, but its value increases upon increasing ε_w. This behavior and the values of both plateaus indicate that the collapsed globule has a very elongated shape.

Finally, in order to conclude the discussion of transitions upon decreasing the temperature at fixed values of adsorption strength ε_w, we have looked at the temperature dependencies of the shape parameters K_1 and K_2 (Figure 6). Again, one can find different behavior for the values of parameter ε_w below and above the value $\varepsilon_w = 1$. For low adsorption strength we observe a sharp change of the parameter K_1 from the value about 0.27 to the value about 0.5–0.65 upon decreasing T, while there is almost no change of the parameter $K_2 \approx 0.88$. This corresponds to a transition from an elongated ellipsoidal object to a much more spherical one. Contrary to this, for the values $\varepsilon_w \geq 1$ there are two transitions visible. First, there is a smooth shift from the point in the parameter space $(K_1, K_2) \approx (0.27, 0.88)$ to the point $(K_1, K_2) \approx (0.17, 0.84)$, i.e. to a more "flat" disk-like object, while the temperature of this transition increases upon increasing the adsorption strength. This is the adsorption transition from a three-dimensional coil to an adsorbed quasi-two-dimensional coil or



a)

b)

Figure 6.

Temperature dependence of the shape parameters, K_1 (a) and K_2 (b), for a semiflexible mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at an adsorbing wall for different values of adsorption parameter ε_w as indicated in the legend.

globule. Then, upon the further decreasing of T we observe a very sharp change of both shape parameters to the point in the parameter space $(K_1, K_2) \approx (0.07, 0.94)$, i.e. to a very elongated cylinder-like object.

This analysis allows to reveal two different transition scenario upon decreasing temperature. For small values of adsorption strength, $\varepsilon_w = 0$ and 0.5, the transition from a coil to a spherical globule (liquid or solid one) takes place. For large values of adsorption strength, $\varepsilon_w \geq 1$, we observe first the adsorption transition from a coil to a quite flat (disk-like) structure and then the transition to a very elongated cylinder-like object.

Let us now look at the transition between the solid crystalline globule and the cylinder-like liquid-crystalline globule (regions III and V on the diagram of state, Figure 1). We fix a low value of the temperature $T = 0.7$ and follow the path along increasing adsorption strength ε_w.

To understand this transition we should analyze the orientational intraglobular ordering of bond vectors. In Figure 7 (left panel) the dependencies of three eigenvalues η_1, η_2, η_3 of the bond vectors orientation tensor (Equation (10)) on the adsorption strength ε_w are shown.

Our semiflexible chain does not show any pronounced internal orientational ordering of bond vectors in the collapsed state in the case of a weakly adsorbing surface, $\varepsilon_w = 0$ and 0.5 (this means that we used the values of parameters which correspond to the case of a moderate stiffness). However, upon increasing the attraction strength ε_w the bond vectors start to orient in the course of adsorption transition. The values of the three eigenvalues of the bond vectors orientation tensor are equal to $\eta_1 \approx 0.8$, $\eta_2 \approx -0.38$, $\eta_3 \approx -0.42$ for $\varepsilon_w \geq 2$ this indicating the preferred orientation of bond vectors along one axis, i.e. the formation of a cylinder-like structure.

On the dependence of the shape parameters on the adsorption strength ε_w (Figure 7, right panel) we observe the change of values of both shape parameters from the point in the parameter space $(K_1, K_2) \approx (0.65, 0.88)$, which corresponds to a spherical object, to the point $(K_1, K_2) \approx (0.07, 0.94)$, which corresponds to a very elongated cylinder-like object.

So, we observe the transition from an almost spherical isotropic globule into a highly oriented liquid-crystalline cylinder-like globule. The vertical line in the diagram of states (Figure 1) show only approximate location of the transition between the crystalline (solid) globule having spherical shape (region III) and the quasi-two-dimensional (liquid)-crystalline cylinder-like globule (region V).

These conclusions are confirmed by the snapshots shown in Figure 8. These snapshots were obtained in the following way. From the temperature dependencies of the total energy, gyration radius and the shape parameters we have obtained the values of

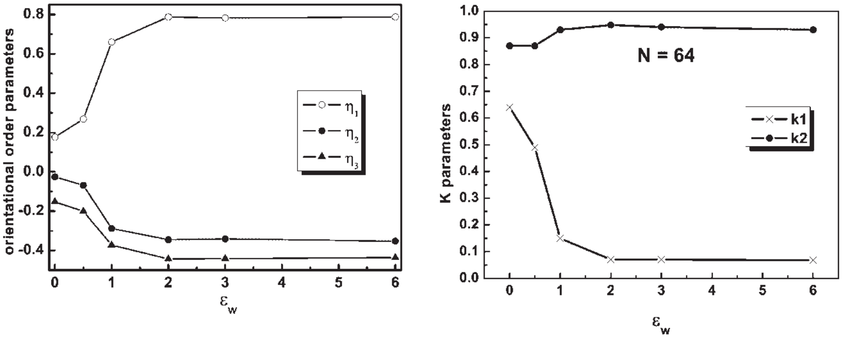


Figure 7.
Dependence of the orientational order parameters (left) and the shape parameters (right) on the adsorption strength parameter ε_w for a semiflexible mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at $T = 0.7$.

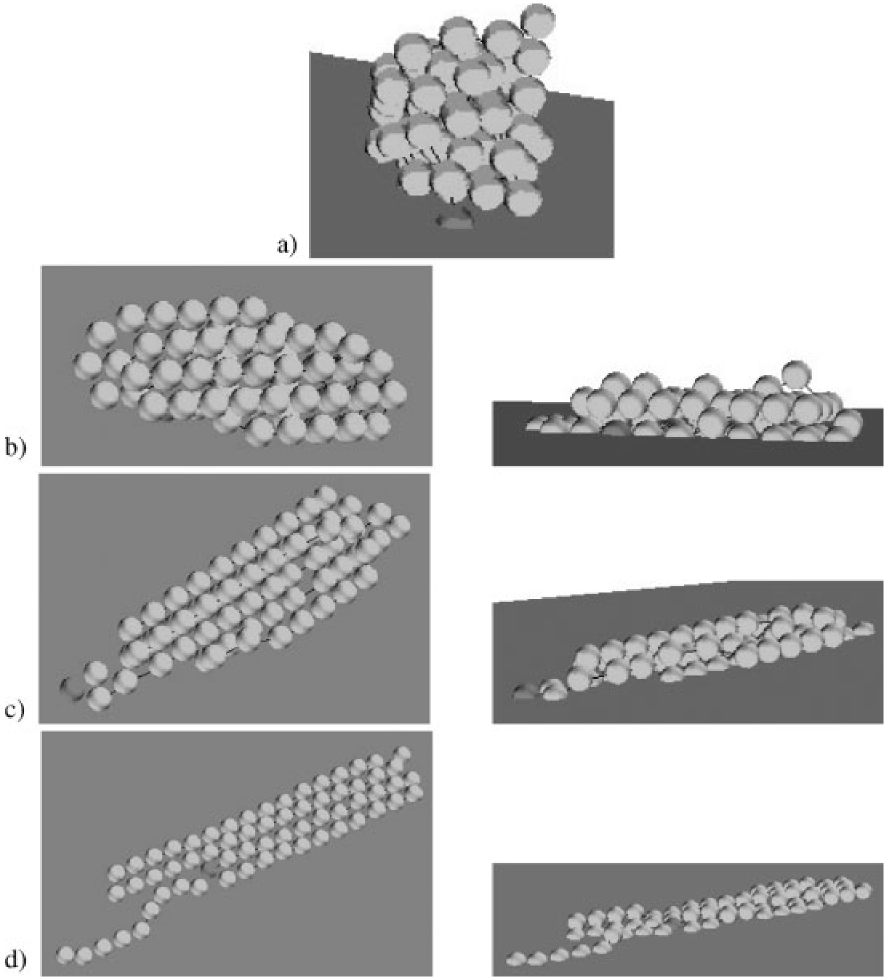


Figure 8.
Snapshots of a semiflexible mushroom chain ($N = 64$, $\varepsilon_\alpha = 4$) at an adsorbing wall having different adsorption strength: $\varepsilon_\alpha = 0$ (a), 1 (b), 2 (c), and 6 (d). Snapshots were obtained at the temperature $T = 0.7$. Both the top (on the left) and the side view (on the right) are presented.

these observable parameters at the temperature $T = 0.7$. Then, we made the search for the conformation having these particular values of observable parameters. From these snapshots it is visible that inside the region V of the diagram of states the cylinder-like globules become flat upon increasing the adsorption strength parameter ε_w.

Concluding Remarks

The diagram of states of a single semiflexible mushroom chain of the length $N = 64$ at a plane adsorbing surface was built by means of lattice Monte Carlo computer simulation using the bond fluctuation model, configurational bias algorithm for chain re-growing and the Wang-Landau sampling technique. Using the computer simulation data for energy, gyration radius, shape parameters and orientational order parameter we have found the regions of stability for a coil, liquid globule, solid isotropic globule, adsorbed coil and cylinder-like liquid-crystalline globule.

Upon increasing the surface attraction strength ε_w the two transitions (the coil–globule and the liquid-solid globule transition) merge together to a single transition from an adsorbed coil to a cylinder-like liquid-crystalline solid globule, i.e. the coil– globule transition disappears at high adsorption strength. It should be mentioned here, that in two dimensions a coil under θ-conditions is undistinguishable from a globule in the sense that the exponent of the power-law dependence of their linear size on the chain length is the same for these two states. We would also like to draw here analogy to the vanishing of the coil–globule transition for the model with short interaction range (see the contribution by W. Paul et.al. in this volume). Actually, the increasing of the adsorption strength leads to an effective reducing of the dimensionality of the polymer chain conformation, and this seems to lead to an effective decreasing of the interaction range.

Another interesting conclusion is that for a semiflexible chain the presence of an attracting wall shifts the equilibrium towards the formation of cylinder-like globules with internal liquid-crystalline ordering of bonds. An open question for further investigations is whether a transition from a three-dimensional cylinder-like liquid-crystalline globule to a two-dimensional cylinder-like liquid-crystalline globule can be identified for larger chain lengths.

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