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Intramolecular structures in a single copolymer chain consisting of flexible and semiflexible blocks: Monte Carlo simulation of a lattice model

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Abstract. We study conformational properties of a single multiblock copolymer chain consisting of flexible and semiflexible blocks. Monomer units of different blocks are equivalent in the sense of the volume interaction potential, but the intramolecular bending potential between successive bonds along the chain is different. We consider a single flexible-semiflexible regular multiblock copolymer chain with equal content of flexible and semiflexible units and vary the length of the blocks and the stiffness parameter. We perform flat histogram type Monte Carlo simulations based on the Wang-Landau approach and employ the bond fluctuation lattice model. We present here our data on different non-trivial globular morphologies which we have obtained in our model for different values of the block length and the stiffness parameter. We demonstrate that the collapse can occur in one or in two stages depending on the values of both these parameters and discuss the role of the inhomogeneity of intraglobular distributions of monomer units of both flexible and semiflexible blocks. For short block length and/or large stiffness the collapse occurs in two stages, because it goes through intermediate (meta-)stable structures, like a dumbbell shaped conformation. In such conformations the semiflexible blocks form a cylinder-like core, and the flexible blocks form two domains at both ends of such a cylinder. For long block length and/or small stiffness the collapse occurs in one stage, and in typical conformations the flexible blocks form a spherical core of a globule while the semiflexible blocks are located on the surface and wrap around this core.

1. Introduction

The collapse transition of a single flexible or semiflexible homopolymer macromolecule has been studied in detail by means of theoretical methods [1–9], computer simulations [10–18], as well as experiments [19–21]. Upon decreasing the solvent quality a single flexible macromolecule undergoes a transition into a structureless compact globule [22–24], while the stiff-chain (semiflexible) homopolymers collapse into structured globules, for example, into toroidal or cylindrical structures [6–8,14,23,25–27]. The complete diagram of states for a single semiflexible homopolymer macromolecule was investigated in Refs. [18,23,28,29]. The stability regions of the coil, the isotropic liquid globule, the crystalline isotropic globule, and the toroidal and cylindrical globule have been found. In these studies of homopolymer chains the stiffness along the chain was assumed to be homogeneous.

Such a model with uniform stiffness describes real macromolecules, but there are many examples where it is important to study the behavior of macromolecules which are heterogeneous in terms of rigidity. One such example are polymers for organic electronics [30]. Also, many biopolymers consist of flexible (coiled) and rigid parts (e.g., α-helices, β-sheets) and form a stable spatial structure, which is also achievable kinetically [31]. Such conformations of polymers can be studied using a model with rigid and flexible chain parts. Previously, this model was used to simulate intramolecular structures in Refs. [33, 34], but in those studies the volume interaction parameter of flexible and rigid blocks was also different. However, a systematic study of the phase diagram of a polymer chain consisting of flexible and rigid blocks, which are identical in terms of volume interaction, still has to be performed. Such a study could show the general trends of the behavior of macromolecules with non-uniform stiffness distribution along the chain and possible structures which can be formed in various conditions. In this contribution we have started a systematic investigation of the behavior of the chain of length 64 monomer units consisting of rigid and flexible parts. We have performed Monte Carlo simulations on a cubic lattice using the bond fluctuation model. The length of the rigid and flexible blocks was equal to each other, and the composition was 1:1. We have studied macromolecules with block length from 4 to 32 monomer units and considered different values of stiffness of the rigid (semiflexible) block.

2. Model and Simulation Technique

In our simulation we have used the standard bond fluctuation model [35]. In this model each monomeric unit of a chain of length N is represented as an elementary cube on the simple cubic lattice, blocking all 8 sites at the corners of this cube from further occupation. The lattice spacing $a \equiv 1$ is taken as the unit of length. The length of the bonds between monomeric units can take the values $2, \sqrt{5}, \sqrt{6}, 3$, and $\sqrt{10}$. The set of bonds consists of 108 different bond vectors, and 87 different angles between subsequent bonds can occur. We have studied a single copolymer chain composed of an alternating sequence of flexible (A) and semiflexible (B) blocks of monomer units. The total length of the chain was equal to 64 monomer units. The block length was varied from 4 to 32, i.e., half of the chain length (diblock copolymer). To model the chain stiffness, we introduced a bending potential depending on the angle θ between subsequent bond vectors l_i and l_{i+1},

$$U_{bending}(\theta) = \varepsilon_\alpha(\cos\theta + 1), \tag{1}$$

where $\varepsilon_\alpha = \varepsilon_{\alpha A} = 0$ for the A monomer units, and $\varepsilon_\alpha = \varepsilon_{\alpha B}$ for B monomer units. The stiffness parameter $\varepsilon_{\alpha B}$ is varied from 4 to 16 (in units of $k_B T$) with step 4 for long blocks in the copolymer.

To model the quality of the solvent, we introduce an attractive square well potential between all monomer units (A and B monomers are equivalent in the sense of the volume interaction potential) which are less than $\sqrt{6}$ lattice units apart in space:

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

where $\varepsilon \equiv 1$ in units of $k_B T$. This potential $U_{contact}$ was applied also between monomer units adjacent along the chain, and there was no potential on the bond length between these monomer units.

We have performed our simulations in a cubic box of size $150 \times 150 \times 150$ with periodic boundary conditions. To change the conformation of the chain we used local moves of monomer units as well as rearrangements of large parts of the chain by means of the configurational bias (CB) algorithm [36]. Additionally, we have implemented the Wang-Landau (WL) sampling

technique [37] to estimate the density of states $g(E)$. Then, for all moves, the acceptance probability p_{acc} was equal to

$$p_{acc} = \min\{1, g(E_{old}/g(E_{new})\} \tag{3}$$

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

For CB moves, the following procedure was used. A monomeric unit i^* and the part of the chain (from the first monomer unit of the chain until unit i^* or from the unit i^* until the end of the chain) was chosen at random, and the selected part of the chain was removed. For such a trial move, one starts from the end and counts the number $k_i^{(old)}$ of free (unoccupied) lattice sites where the considered monomer i could potentially be located (respecting bond constraints). Then, the next monomer is treated analogously, and so forth, until i^* is reached. Then, we attempt to regrow the removed part of the chain in a new conformation, choosing at every step of the growth attempt the position of the next monomeric unit i at random out of the $k_i^{(new)}$ possible lattice sites that comply with excluded volume and bond length constraints. At the end of this regrowth trial, we calculate weights of the old and the new conformations

$$w_{new} = \prod_{i=i^*+1}^{N} k_i^{(new)} \qquad w_{old} = \prod_{i=i^*+1}^{N} k_i^{(old)}. \tag{4}$$

Finally, the trial move is accepted with probability

$$p_{acc}(CB) = \min\{1, [g(E_{old})/g(E_{new})](w_{new}/w_{old})\}. \tag{5}$$

We divide the whole interval of the total energy, E, in sub-intervals (windows) of width about 200. We start the simulation in each window with $g(E) \equiv 1$ for all values of E. We accumulate the histogram, $H(E)$, of visits to energy E and simultaneously update the density of states $g(E)$ (multiplying it by a factor f) until the histogram $H(E)$ becomes flat within the pre-defined deviation (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 factor f (we start with the initial value $f = e$ and take the square root of the modification factor f after each iteration) 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 $H(E)$ to zero. We stop the iteration procedure after f reaches the value 1.0000001 and perform the productive simulation run with the obtained density of states $g(E)$ in order to accumulate the histograms of observable parameters. Then, the density of states $g(E)$ is used to calculate the temperature dependencies of average values of the 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 a wide region of temperatures using the following re-weighting formulas:

$$\langle E \rangle (T) = \frac{1}{Z(T)} \sum_E E g(E) e^{-E/k_B T} \tag{6}$$

$$Z(T) = \sum_E g(E) e^{-E/k_B T} \tag{7}$$

$$\left\langle R_G^2 \right\rangle (T) = \frac{1}{Z(T)} \sum_E \overline{R}_G^2(E) g(E) e^{-E/k_B T}, \tag{8}$$

where $\overline{R}_G^2(E) = \sum_{conf,E} R_G^2 / \sum_{conf,E} 1$, i.e., the average gyration radius over conformations with given value of the total energy E calculated using the histogram file accumulated in the course of the productive simulation run.
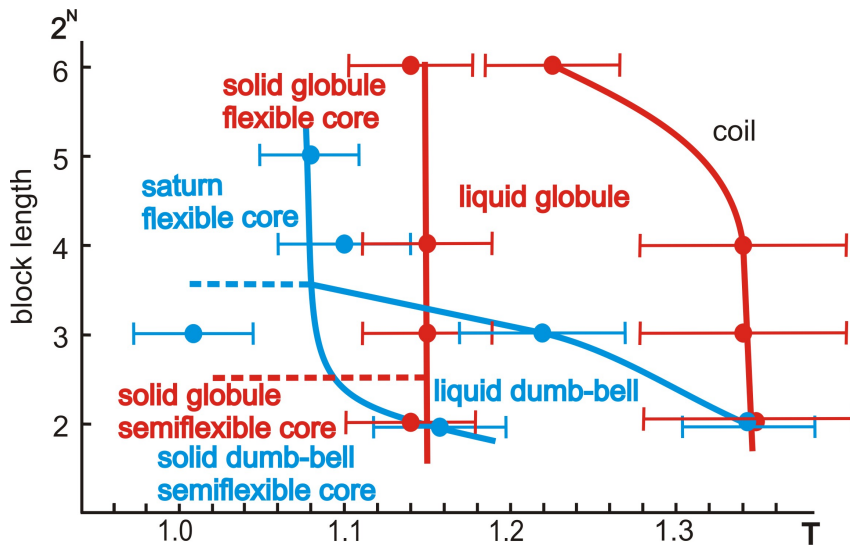
Figure 1. Diagram of states for the chain length 64 monomer units in varables block length (presented as power of 2) vs. temperature. Red colour is for $\varepsilon_{\alpha B} = 4$, blue color is for $\varepsilon_{\alpha B} = 8$.

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

$$Q_{\alpha\beta} = \frac{1}{N-1} \sum_{i=1}^{N-1} \frac{1}{2} \left(3 \left\langle e_i^\alpha e_i^\beta \right\rangle - \delta_{\alpha\beta} \right), \tag{9}$$

where e_i^α 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 $i+1$.

For this model the phase diagram for flexible chains has been determined using the Wang-Landau simulation method [38], and the state diagram of semiflexible chains has been determined by means of expanded ensemble simulation techniques [23].

3. Results and discussion
We have obtained a preliminary diagram of states (fig. 1) for the flexible-semiflexible block copolymer chain in variables block length vs. temperature. The block length is presented as a power of 2. The points with error bars indicate the simulation data while the solid and dashed lines are guides for the eye. The diagram of states for $\varepsilon_{\alpha B} = 4$ is shown in red colour, and that one for $\varepsilon_{\alpha B} = 8$ is shown in blue colour. For the flexible homopolymer chain the temperature of the liquid-solid globule transition is equal to $T \approx 1.18$, as has been calculated in our previous work [23].

For the high temperature we observe, of course, coil conformations for both values of the stiffness parameter of semiflxible blocks. Upon decreasing temperature, the coil–globule transition occurs first, and it is followed by the transition between liquid globule and solid globule at lower temperatures. One can see the difference between the chains with different stiffness of semiflexible blocks ($\varepsilon_{\alpha B} = 4$ and $\varepsilon_{\alpha B} = 8$). The most obvious difference is that there is only a single transition between the coil and globule states for the chains with $\varepsilon_{\alpha B} = 8$ and large block length.

Now let us discuss the structure of the solid globule which appears to be quite different for the chains with short and long block length for both values of the stiffness parameter. For a more flexible chain (with $\varepsilon_{\alpha B} = 4$), the solid globule has approximately spherical shape but for

short block length the globular core is formed by semiflexible blocks (while the flexible blocks form the shell) and for long block length (more than 8 monomer units in one block) the core is formed by flexible blocks (while the semiflexible blocks form the shell). In case of $\varepsilon_{\alpha B} = 8$, for the long block length only one transition occurs (like for the large stiffness of a hompolymer chain). There is a transition from coil to "saturn" like globule [39] with a flexible core (like for the case of $\varepsilon_{\alpha B} = 4$ and long blocks). With decreasing the block length we observed a two stage transition: first, the transition from coil to liquid dumbbell globule, and second, the transition to solid dumbbell globule which has a semiflexible core. The location of the transition between these two different types of intraglobular monomer packing (semiflexible core vs. flexible core) is indicated by the horizontal dashed line for both values of the stiffness parameter.

In fig. 2 we present some conformations for the chain of length 64 monomer units for different block length and different values of the stiffness parameter, and transition temperatures are indicated in this figure as well. Semiflexible blocks are shown using red colour, the flexible ones using green colour. Transition temperatures were defined from maxima in the temperature dependence of the full energy fluctuations. The temperature dependence of the contact energy looks very similar to that of the full energy, but the positions of the fluctuation maxima are slightly different. In fig. 2a) wee see a spherical globule with semiflexible core and in figures b) and c) the core is composed by flexible blocks of monomer units.

The criteria for determining the structure of conformations were the contact energy and the gyration radius (of the whole chain and of different blocks separately). In fig. 3 and fig. 4 the temperature dependence of the contact energy is shown. In this figure, the black lines are for the total contact energy, the red ones for contacts between monomer units of flexible blocks, the green ones for contacts between monomer units of semiflexible blocks and the blue ones for contacts between monomer units of flexible and semiflexible blocks (the estimated error in these curves is less than one percent). As one can see, with increasing the block length from 4 monomer units (fig. 3) to 8 monomer units (fig. 4) the red and green lines change their positions. For short blocks the monomer units of semiflexible blocks are more compact (have more contacts) while for longer blocks the flexible blocks are more compact (have more contacts). This confirms that the globule has a semiflexible core for short blocks and a flexible core for longer blocks. The same situation is observed for chains with $\varepsilon_{\alpha B} = 8$. For short blocks we find dumbbell conformations (fig. 2 d) and e)) where semiflexible blocks form a cylinder-like globule as a core, and flexible ones form two spherical globules at both ends of the cylinder-like core. For long blocks (fig. 2 f) and g)) we see "saturn"-like morphologies with a flexible core while the semiflexible blocks are located on the surface and wrap around this core.

The collapse occurs in two stages for small stiffness and for short blocks for larger stiffness. In fig. 5 wee see two maxima for the fluctuations of the total contact energy (black curve), indicating two stages of the collapse. The right maximum corresponds to the coil – liquid globule transition and the left one to the liquid – solid globule transition. Earlier, we have shown [23] that, similarly, for homopolymer macromolecules with large stiffness parameter the collapse transition occurs as a single transition while for smaller stiffness parameter it occurs in two stages.

4. Conclusions

We have studied conformational properties of a single multiblock copolymer chain consisting of flexible and semiflexible blocks and obtained different non-trivial globular morphologies for different values of the block length and the stiffness parameter. Our conlcusion is that the collapse can occur in one or in two stages depending on the values of both these parameters. For short block length and/or large stiffness the collapse occurs in two stages, because it goes through intermediate (meta-)stable structures, like a dumbbell shaped conformation. In such conformations the semiflexible blocks form a cylinder-like core, and the flexible blocks form two
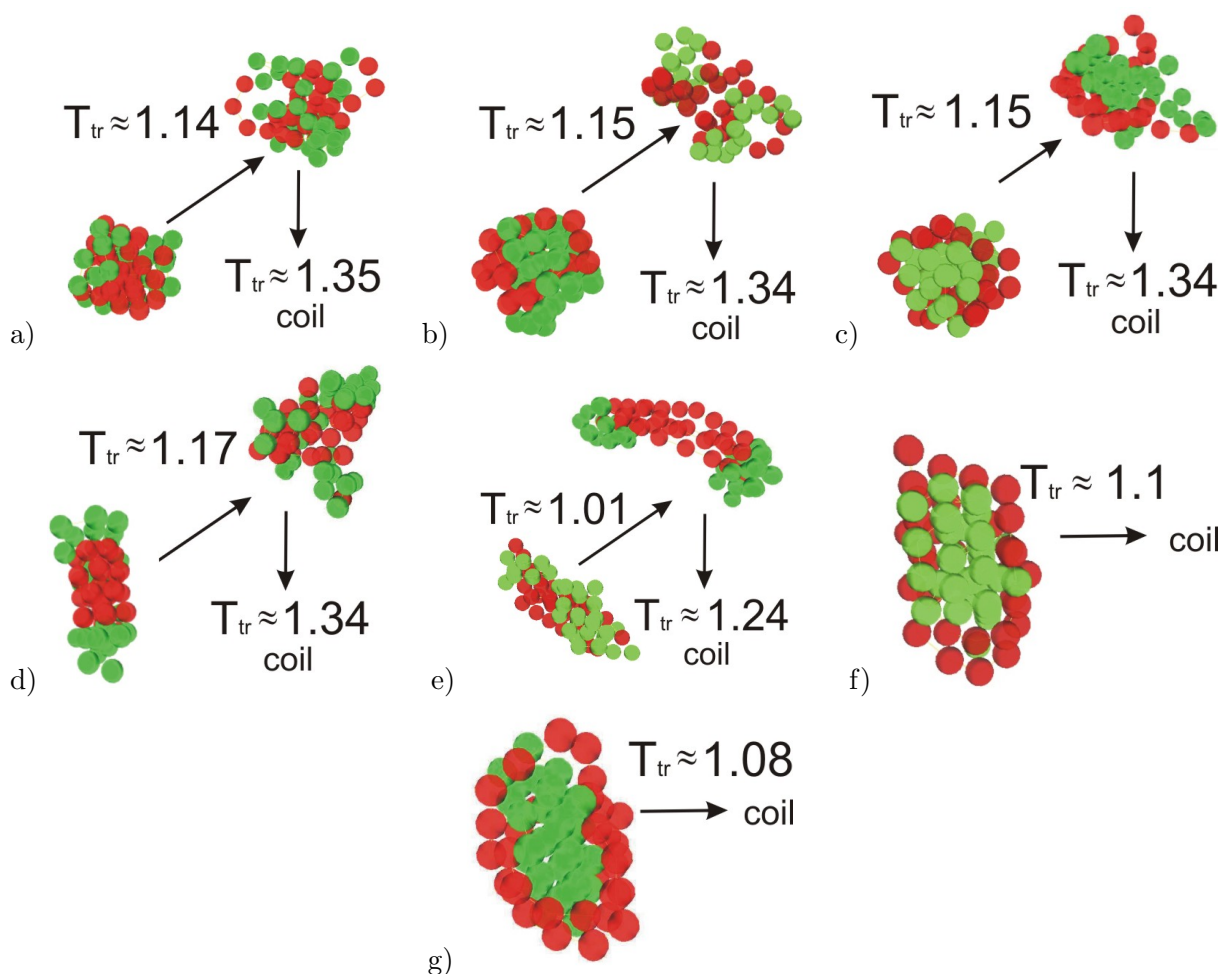
Figure 2. Conformations observed for the chain length 64 monomer units for semiflexible blocks (shown in red colour) with $\varepsilon_{\alpha B} = 4$: a) block length equal to 4 monomer units; b) block length equal to 8 monomer units; c) block length equal to 16 monomer units; for semiflexible blocks with $\varepsilon_{\alpha B} = 8$: d) block length equal to 4 monomer units; e) block length equal to 8 monomer units (dumbbell like conformation); f) block length equal to 16 monomer units ("saturn"-like conformation); g) block length equal to 32 monomer units ("saturn"-like conformation).

domains at both ends of such a cylinder. For long block length and/or small stiffness the collapse occurs in one stage, and in typical conformations the flexible blocks form the spherical core of a globule while the semiflexible blocks are located on the surface and wrap around this core ("saturn"-like conformations). Keeping the stiffness parameter of the semiflexible blocks to be constant and varying the block length we can observe the intraglobular structural transition from dumbbell to "saturn"-like conformations. To check whether these conclusions will be also valid for longer chains, we are now studying the chains consisting of 256 monomer units.
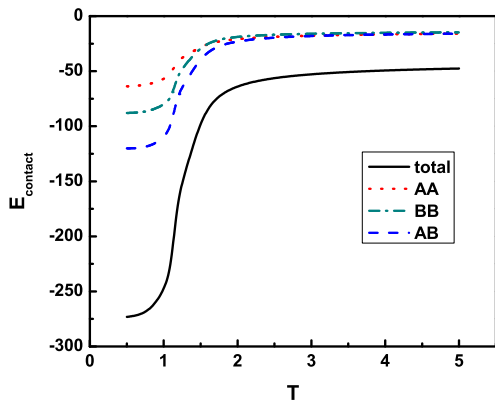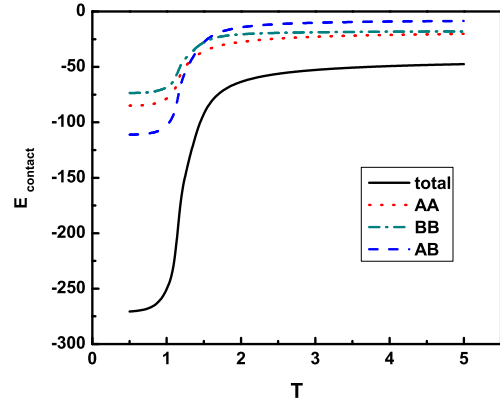
Figure 3. Contact energy (total contacts, AA-, BB- and AB-contacts) for the chain of length 64 monomer units consisting of alternating blocks of 4 monomer units, $\varepsilon_{\alpha B} = 4$.
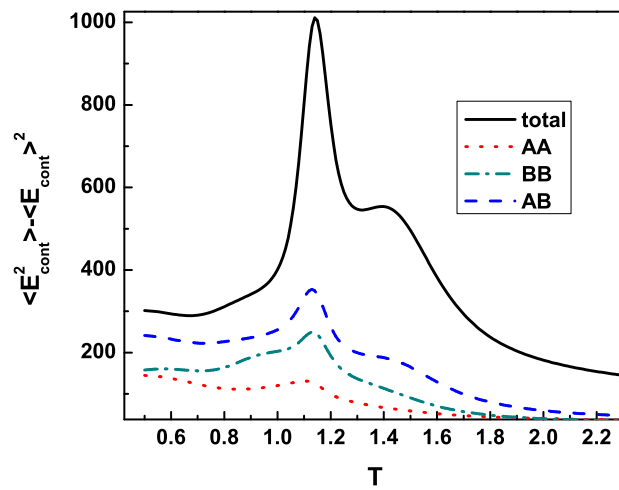
Figure 4. Contact energy (total contacts, AA-, BB- and AB-contacts) for the chain of length 64 monomer units consisting of alternating blocks of 8 monomer units, $\varepsilon_{\alpha B} = 4$.

Figure 5. Fluctuations of contact energy (total contacts, AA-, BB- and AB-contacts) for the chain of 64 monomer units consisting of blocks of 4 monomer units, $\varepsilon_{\alpha B} = 4$.

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