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Probing the effect of density on the aggregation temperature of semi-flexible polymers in spherical confinement

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Abstract

Applying parallel multicanonical simulations, we study the aggregation transition of finite semi-flexible polymers in dependence on the density, where we keep the polymer length fixed as a chemical property. A spherical confinement is imposed to constrain the translational entropy. We show that the competition between single-polymer collapse and many-polymer aggregation yields a lower temperature bound for the isolated chain approximation. For dilute semi-flexible polymers, we present entropic arguments that allow to relate the inverse aggregation temperature to the density of the uniform polymer system.

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Keywords: aggregation; segregation; multicanonical simulations; polymer stiffness; spherical confinement

1. Introduction

In nature, proteins or polymers are often encountered in geometrical confinement, e.g., in cellular environment or porous media. These external constraints alter the physics of the system significantly. One prominent example is the change of both dynamical and structural properties when folding in chaperones. The impact of spherical confinement on the linear extension of polymers in good solvent has been studied recently by different means, see Sakaue and Raphaël (2006); Cacciuto and Luijten (2006); Jun et al. (2007), which led to insight into the connection between semi-dilute solutions and the free energy of a single polymer. A single flexible θ-polymer caged in a sphere has been investigated by Marenz et al. (2012), where it was shown that the transition temperature of the θ-collapse is shifted with the radius of the surrounding sphere. A similar exercise was conducted very recently by Zierenberg et al. (2014) with the focus on the impact of a confining sphere onto the aggregation transition and its dependence on the density. Here, we will follow the latter work to some extent and present peculiarities arising from the stiffness of polymers in such a system.

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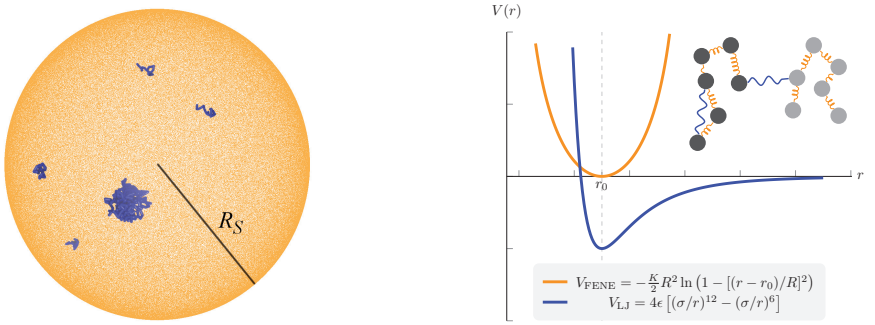

Fig. 1. Sketch of the model: M polymers are enclosed in spheres with different radii R_S. Each polymer consists of N monomers, which interact either via a FENE potential if they are bonded or a Lennard-Jones potential if they are non-bonded. For the Lennard-Jones interaction only two representatives are drawn to show that the potential parametrizes both intra- and interpolymer interactions.

2. Model and Method

The system comprises M uniform polymers without any side chains and each polymer consists of N monomers. Given the spatial coordinates of the monomers $\vec{r}_i$, $i = 1, \ldots, M \times N$, the interaction between two *non-bonded* monomers i, j at a distance $r = |\vec{r}_i - \vec{r}_j|$ is approximated by a 12-6 Lennard-Jones potential,

$$V_{\mathrm{LJ}}(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right]. \tag{1}$$

The two free parameters ϵ and σ determine the interaction strength and the distance, where the interaction changes from being repulsive to being attractive. As a slight modification, the Lennard-Jones potential is cutoff and shifted at $r_c = 2.5\sigma$, so that it vanishes for $r > r_c$. The modified potential is continuous at $r = r_c$, the qualitative behaviour is not changed and a considerable speed-up of simulations is enabled. The free parameters of the potential are chosen to be consistent with the investigations by Milchev et al. (2001); Schnabel et al. (2009); Zierenberg et al. (2014); and Zierenberg and Janke (2015), namely, $\epsilon = 1$ and $\sigma = r_0/2^{1/6}$. The distance $r_0 = 0.7$ sets the typical bond length of *bonded* monomers that interact via a finitely extensible nonlinear elastic (FENE) potential,

$$V_{\mathrm{FENE}}(r) = -\frac{K}{2}R^2 \ln\left(1 - [(r - r_0)/R]^2\right), \tag{2}$$

mimicking the springs between monomers of the same polymer. The remaining parameters of the FENE potential are $R = 0.3$ and $K = 40$ in compliance to the aforementioned literature. Furthermore, stiffness is introduced as a penalty from the discretized polymer curvature which leads to an effective bending potential,

$$V_{\mathrm{bend}}(\theta) = \kappa(1 - \cos\theta), \tag{3}$$

where θ is the angle between consecutive bond vectors. We consider in the following two cases with length $N = 13$: flexible polymers with $\kappa = 0$ and an example of rather stiff polymers with $\kappa = 9$.

Apart from the implicit internal constraints like excluded volume effects arising from the repulsive term in the Lennard-Jones potential and bending stiffness, we introduce an external constraint to the whole system by confining it to a sphere of radius R_S. This setup offers a suitable way for the study of density effects in finite or mesoscopic systems: the steric inner wall yields at most an effective repulsive interaction and a systematic variation of the radius changes the density in a controlled way. An illustrative overview of the system is given in Fig. 1.

As we are interested in aggregation, a process which shows characteristics of a first-order phase transition, we employ Markov Chain Monte Carlo simulations in the multicanonical ensemble, developed by Berg and Neuhaus (1991, 1992). This probabilistic algorithm has been applied to systems with phases that are separated by large barriers, for example by Janke (1992, 1998a). The main idea of the algorithm is the artificial support of suppressed, unlikely states by a well-defined procedure that can be reversed at the end. This allows one to overcome entropic or energetic barriers fast and at the same time enables us to calculate estimators of observables in the canonical or microcanonical ensemble. To further reduce the wall-clock time we use a parallelized version that was proposed and tested by Zierenberg et al. (2013) which shows an almost perfect speed-up. We apply the algorithm with up to 256 cores.