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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.

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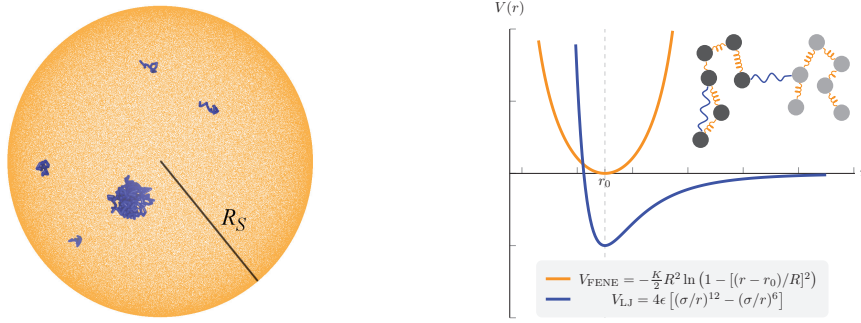
Fig. 1. Sketch of the model: M polymers are enclosed in spheres with different radii R_S. Each polymer consists of N monomers, which interact either via a FENE potential if they are bonded or a Lennard-Jones potential if they are non-bonded. For the Lennard-Jones interaction only two representatives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

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

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,

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

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,

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

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.
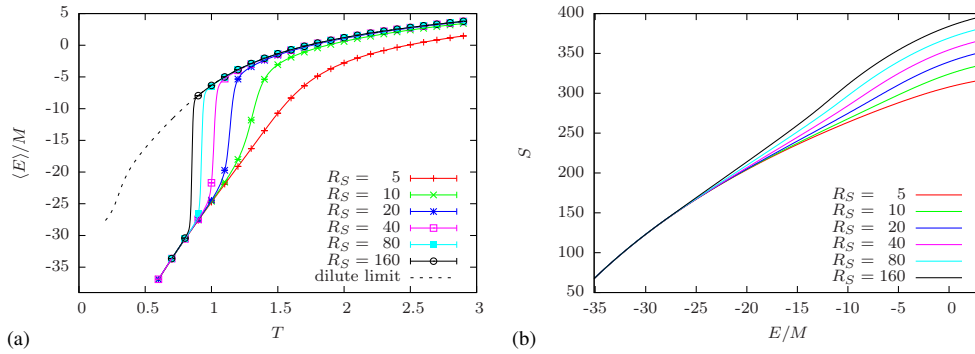
Fig. 2. Results for $M = 8$ flexible polymers of length $N = 13$ in a confining sphere of radius R_S. (a) The normalized energy as a function of temperature. With increasing radius (decreasing density) the aggregation temperature is lowered systematically. (b) Microcanonical entropy (up to an additive constant) obtained from a microcanonical analysis of the multicanonical data.

The transition between different configurations is mediated by a set of various update moves, including single-bead displacement, bond rotation, translation of the center of mass of a polymer and a double-bridging move. The range of the translational update of the polymers is coupled to the radius of the confining sphere to counter the increasing entropy. The update ranges of single-bead displacement and bond rotation moves are chosen in dependence of the system's internal energy to optimize fast traveling of the system through a broad range of energies. All those moves are implemented in the same spirit as in earlier simulations by Schnabel et al. (2011) to assure detailed balance. During the production run the best estimate on the multicanonical weights are fixed and the system is thus kept in equilibrium. The data from the actual production run is reweighted to yield canonical or microcanonical statistics.

3. Results

In Fig. 2(a) we show the energy as a function of the temperature obtained by our method for $M = 8$ polymers, each composed of $N = 13$ monomers. The sharp jumps expose the aggregation transition. Here, with increasing temperature T the system changes from a regime of a single macroscopic object surrounded by a fraction of "free" polymers to a gas-like, homogeneous regime of individual polymers. For the numerical determination of the transition temperature, we use the derivative of the energy with respect to the temperature, the specific heat per polymer, $C_V/M = \left(1/k_B T^2\right)\left(\langle E^2\rangle - \langle E\rangle^2\right)/M$ with $k_B = 1$ in the following. This shows a pronounced peak at the aggregation transition temperature which can be used for a well-defined identification of the transition temperature of the finite system. As already discussed in greater detail by Zierenberg et al. (2014), the transition temperature shifts towards lower temperatures with increasing radius of the confining sphere.

The microcanonical ensemble enables us to quantify this effect. The entropy then is the logarithm $S(E) = \ln \Omega(E)$ of the total number $\Omega(E)$ of states with a given energy E (up to an additive constant). The estimator from our simulations is plotted in Fig. 2(b). The entropy $S(E_{\text{agg}})$ of the states in the aggregated phase is barely influenced by the confinement in contrast to the separated phase. We can approximate the number of states of the separated phase $\Omega(E_{\text{sep}}) \propto V^M$, where $V = (4\pi/3) R_S^3$ is the volume of the confining sphere that is accessible to the system. Therefore, with the polymer density $\rho = M/V$ the entropy reads

$$S(E_{\text{sep}}, \rho) \sim \ln\left[V^M\right] = \ln\left[\left(\frac{M}{\rho}\right)^M\right] = -M\left(\ln \rho - \ln M\right) , \tag{4}$$

and, for fixed M, this leads to a logarithmic dependence of the microcanonical aggregation temperature on the density,

$$1/T_{\text{agg}}(\rho) = \frac{S(E_{\text{sep}}, \rho) - S(E_{\text{agg}}, \rho)}{\Delta E} \sim \frac{S(E_{\text{sep}}, \rho)}{\Delta E} = \frac{S(E_{\text{sep}}, \rho)}{M\Delta e} \sim -\ln \rho + \text{const} , \tag{5}$$

with $\Delta E = E_{\text{sep}} - E_{\text{agg}} = M\Delta e$ under the assumption that, for fixed M and N, the latent heat Δe is almost constant. We employed in the first equality in Eq. (5) the notion of the microcanonical aggregation temperature. It is the inverse slope
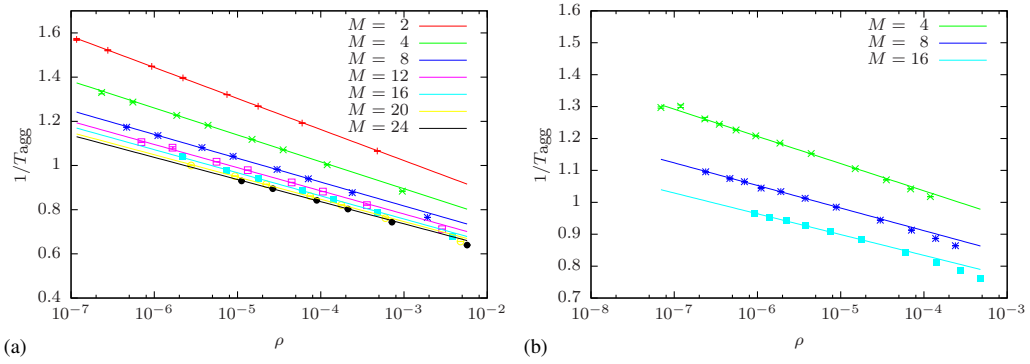
Fig. 3. (a) Dependence of the inverse transition temperature on the density ρ for $M = 8$ flexible ($\kappa = 0$) polymers of length $N = 13$. (b) The same for M rather stiff polymers ($\kappa = 9$; $N = 13$). In both cases the logarithmic dependence of Eq. (5) is clearly visible, for sufficiently small densities.

of the hull connecting the microcanonical entropy of the aggregated and separated regime as is, e.g., discussed in the work of Janke (1998b) and Junghans et al. (2006, 2008, 2009) in detail. The same behaviour from the microcanonical aggregation temperature is expected for the temperature from the peak of the specific heat and confirmed in Fig. 3 for both flexible and rather stiff polymers.

In the case of flexible polymers the aggregate can, in leading order, be treated as a collapsed single polymer of length $N \times M$ which has been exploited by Zierenberg et al. (2014) to find an empirical finite-size scaling for the transition temperature in dependence of the number of polymers $1/T_{\text{agg}} \sim M^{-1/3}$. This holds when a large fraction of polymers contributes to the aggregate and is then valid for a broad range of fixed densities $\rho \in [10^{-7}, 10^{-2}]$ which led to a data collapse in the aforementioned literature. For semi-flexible and stiff polymers the scaling of the typical length scale of the aggregate of polymers does not follow from simply considering one single polymer. This can already be seen in quantities like the so-called "phase" separation parameter,

$$\Gamma^2 = \frac{1}{2M^2} \sum_{\mu,\nu=1}^{M} \left(\vec{r}_\mu^{\ \text{cm}} - \vec{r}_\nu^{\ \text{cm}} \right)^2 , \tag{6}$$

where $\vec{r}_\mu^{\ \text{cm}} = \sum_{i_\mu}^{N} \vec{r}_{i_\mu}/N$ gives the center of mass of the respective polymer μ. By construction, this gives the average squared distance between the polymers and is well-suited to distinguish between the aggregated and separated regimes, see also Junghans et al. (2009) and Zierenberg and Janke (2015) for the case of semi-flexible or stiff polymers. In Fig. 4 the equilibrium average $\langle \Gamma \rangle$ of the square root of Eq. (6) is plotted as a function of the temperature for different radii of the sphere. In the high-temperature regime the parameter saturates at ever increasing values when increasing the radius of the confining sphere. This is expected from the gas-like behaviour in the separated phase where the polymers distribute homogeneously in the available space, independent from the stiffness. However, the aggregated phase gives a smaller value of the phase separation parameter for stiffer polymers. This means that the center of masses must be closer packed for stiff polymers. This can be explained by the observation that flexible polymers tend to dissolve before forming an amorphous aggregate, but stiff polymers form bundles, so the average distance between polymers decreases. Lately these bundles have been investigated by Zierenberg and Janke (2015) and an interesting result is the formation of twisted bundles that can be characterized by measuring additional angle correlations.

4. Conclusion

We have derived that the shift of the inverse aggregation temperature is proportional to the logarithm of the density for a small set of polymers that are confined in a sphere, by considering the polymers as an ideal gas in the separated phase. Furthermore, we have argued that the stiffness of polymers introduces structural changes to the aggregate. Polymer bundles here hamper with the ansatz of the flexible case, so that the derivation of a scaling law that connects the inverse transition temperature to the number of polymers becomes more difficult. With an ansatz for the typical length scale of an aggregate bundle, it should be viable to derive such law in principle.
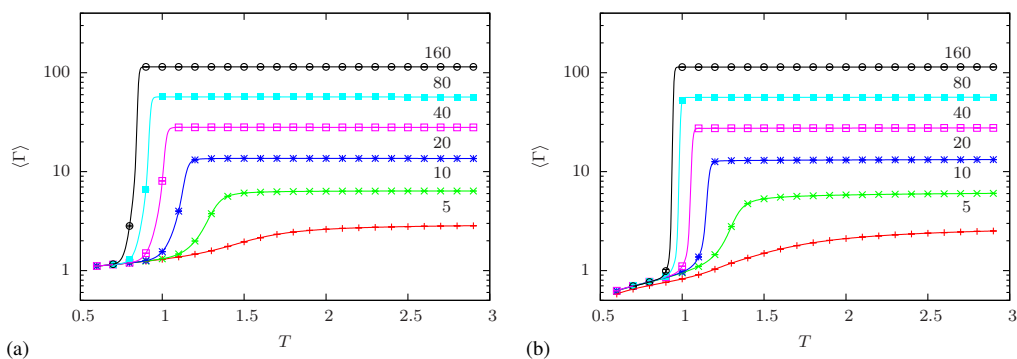
Fig. 4. (a) Phase separation parameter for a system of $M = 8$ flexible polymers of length $N = 13$ in a confining sphere. The radii R_S of the sphere are varied and denoted on the appropriate lines in the plot. (b) The same for rather stiff polymers with $\kappa = 9$.

Acknowledgements

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