

Entropic collapse transition of a polymer in a solvent with a nonadditive potential

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We use molecular dynamics simulations to study an entropy-driven collapse transition of a flexible polymer in a solvent. Monomers and solvent particles interact with a steeply repulsive soft-sphere potential. We consider a nonadditive potential system in which the effective diameter describing the solvent-monomer interaction is greater than or equal to the diameters corresponding to the solvent-solvent and monomer-monomer interactions, which are set equal. We examine the effects of nonadditivity of the solvent-monomer potential and solvent density on the collapse transition. We find that a small degree of nonadditivity will drive the transition at sufficiently high solvent density. Increasing the density leads to a collapse transition at lower values of nonadditivity. [S1063-651X(99)06609-X]

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The collapse of a polymer in a solvent from a swollen coil to a compact globule has been the subject of a huge body of experimental, theoretical, and computer simulation research and constitutes an important model system with applications ranging from the stability of polymers to dimixing in a solvent to protein folding. Typically, simulation studies of polymer chain collapse have employed isolated chain models in which the monomer interaction potential is composed of either hard- or soft-core repulsion as well as short-range attraction. The latter component is an effective potential which represents a contribution from the true monomer-monomer potential as well as (and especially) the effect of the solvent medium. While such simple models provide much insight into the polymer collapse problem, they provide little or no understanding about how the microscopic details of the solvent and its interaction with the polymer determine the stability of the chain to collapse. Only by explicit inclusion of the solvent molecules can this problem be addressed.

In 1992, Frenkel and Louis proposed that a purely hard-core polymer could undergo an entropy-driven collapse transition in a hard-core (and therefore athermal) solvent [1]. This was presented in the context of an exact result demonstrating an entropic demixing transition of a hard-core binary mixture of particles using a simple lattice model. The polymer collapse transition can be understood as arising from the competition between the conformational entropy of the chain and the translational entropy of solvent, which favor swollen and collapsed chain states, respectively. Soon after this study, the phenomenon was observed in two Monte Carlo simulation studies of lattice chains, first by Dijkstra *et al.* [2,3], and later by Luna-Bárceñas *et al.* [4], who examined the role of solvent size and shape on the transition. In each study, the chain collapse was manifest in the sudden reduction of the radius of gyration R_g upon an increase in the solvent density [2–4] or chain length [3]. The state of a chain, or equivalently, the quality of the solvent, was determined by monitoring the scaling of R_g with chain length N , $R_g \sim N^\nu$, where $\nu \approx 0.58$ for a good solvent (swollen coil) and $\nu = 1/3$ for a poor solvent (collapsed chain).

The simulation of an entropy-driven polymer collapse transition for an off-lattice (i.e., continuous-space) system

has proven to be more difficult. Recently, Escobedo and de Pablo [5] simulated a 32-mer hard-sphere chain in a monomeric hard-sphere solvent, but did not observe a collapse transition for solvent packing fractions up to $\eta = 0.48$, just below the freezing transition of the solvent. Note that in the study of Dijkstra *et al.* [2,3], the polymer collapse was seen only at a very high solvent packing fraction of $\eta = 0.7$ (though results for packing fractions between 0.3 and 0.7 were not reported), a value at which a hard-sphere solvent is in a solid phase. Following this study, the same group reported a successful observation of an entropic collapse transition for a similar athermal hard-sphere chain in a hard-sphere solvent for longer chain lengths, and where the solvent particle diameter σ_{sol} was set to five times that of the monomer diameter [6]. However, the physical picture of this system is that of a polymer-colloid mixture, rather than a standard polymer-solvent system. The transition was observed at chain lengths for which $R_g \approx \sigma_{\text{sol}}$. It remains an open question as to whether a hard-sphere chain in a hard-sphere solvent can undergo an entropy-driven collapse transition at accessible solvent densities when the solvent and monomer diameters are about equal. If so, it will likely occur only when the chains are very long and at high densities.

In the present paper, we consider the effects of nonadditivity of the solvent-polymer potential in a system similar to those described in the studies cited above. It is well known that, at sufficiently high densities, a symmetric binary fluid mixture composed of hard spheres of equal diameter, but for which the effective diameter between spheres of different species is larger, undergoes demixing into two phases that are each rich in one of the two species. It is possible that employing a nonadditive solvent-monomer potential in the chain-solvent system could induce an analogous microphase separation, i.e., chain collapse. In fact, the (lattice) model system discussed in the article by Frenkel and Louis [1], which introduced the possibility of an entropy-driven collapse transition, employed an effectively nonadditive hard-core potential. We demonstrate that a continuous (i.e., off-lattice) chain-solvent system with a nonadditive potential, in which unlike species (monomer and solvent) interact with an

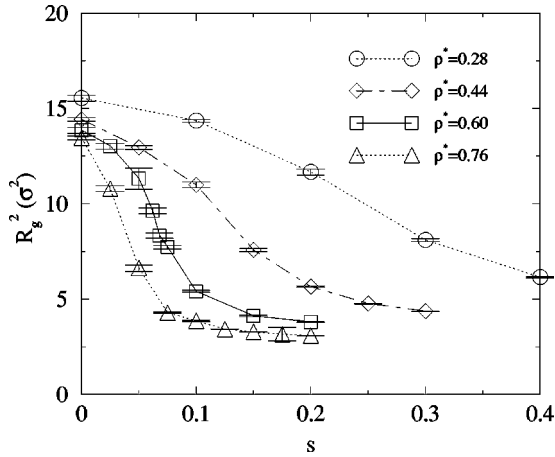


FIG. 1. Mean-square radius of gyration R_g^2 vs nonadditivity s for a polymer of length $N=40$ at pressures $P^*=1.0, 2.5, 5.0,$ and 10.0 , which correspond to densities of $\rho^*=0.28, 0.44, 0.60,$ and 0.76 , respectively, for pure solvent.

effectively larger diameter than do like species, does indeed undergo an entropy-driven transition to a collapsed chain state.

We employ isothermal-isobaric (N - P - T) molecular dynamics simulations to study an isolated chain immersed in a solvent. Monomer-monomer and solvent-solvent interactions are described by a steeply repulsive potential, $u_{mm}(r) = u_{ss}(r) = \epsilon(\sigma/r)^n$, where $n=30$. The monomer-solvent interaction potential is given by $u_{ms}(r) = \epsilon[\sigma/(r-s\sigma)]^n$, where s is the degree of nonadditivity of the potential. Although the system is not rigorously athermal, the steeply repulsive nature of the site-site potentials should make an excellent approximation to the hard-particle limit. Finally, adjacent monomers on the chain were bonded with a harmonic potential $u_{\text{bond}} = k_b(r-\sigma)^2/2$, where $k_b\sigma^2/\epsilon=500$.

The simulations were carried out at a temperature of $T^* \equiv k_B T/\epsilon = 2.0$, and at pressures of $P^* \equiv P\sigma^3/\epsilon = 1.0, 2.5, 5.0,$ and 10.0 , which correspond to solvent densities of $\rho^* \equiv N_s\sigma^3/V = 0.28, 0.44, 0.60,$ and 0.76 , respectively, in the case of pure solvent. The simulations used a range of chain lengths up to $N=50$ monomers at $\rho^*=0.28$ and $N=40$ at higher solvent densities, and with up to $N_s=1678$ solvent particles, though fewer solvent particles were used with shorter chains. The number of solvent particles was chosen for a particular density so that the radius of gyration was no greater than a quarter of the simulation box length, in order to avoid artificial monomer-monomer interactions caused by the chain wrapping around the periodic boundaries.

The principal quantity that we monitor is the root-mean-square radius of gyration R_g as a function of chain length N , solvent density ρ^* , and nonadditivity s . In order to obtain statistically meaningful estimates of this quantity, the system was run for times much longer than the time scale of the fluctuations in R_g , which increases rapidly with increasing chain length and solvent density. Typically, we equilibrated the system for $\Delta t^* \equiv (\epsilon/m\sigma^2)^{1/2}t = 2000$ and sampled the data for $\Delta t^* = 10000$, though $\Delta t^* = 20000$ was sometimes used for the longer chains. With a time step of $\delta t^* = 0.005$, this corresponds to $(2-4) \times 10^6$ time steps.

Figure 1 shows R_g^2 as a function of nonadditivity s at various solvent densities for chains of length $N=40$. The

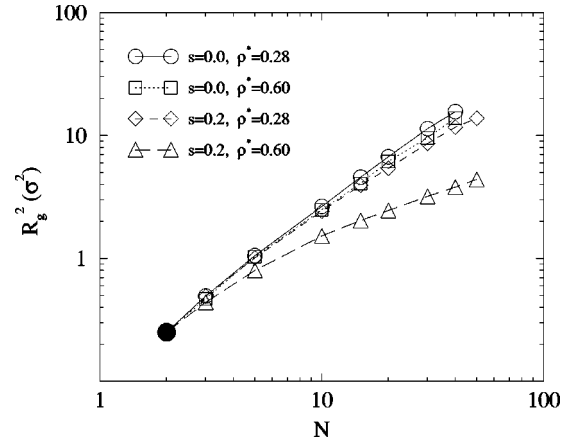


FIG. 2. Mean-square radius of gyration R_g vs polymer length N at various densities and degrees of nonadditivity s .

trend is very clear: there is a consistent decrease in R_g^2 with increasing s at all densities. As the solvent density increases, the decrease occurs more rapidly; that is, the chain collapse occurs more easily (i.e., at lower values of nonadditivity s) with increasing solvent density. The curves are sigmoidal in shape and level off to a constant value at large s . This behavior is reminiscent of the sort of collapse transition seen in model polymer systems when the temperature is varied. The controlling parameter that governs the transition in the present case, s , is analogous to inverse temperature.

In order to show that the system undergoes a true collapse transition, we determine the relationship between R_g and N for different degrees of nonadditivity and solvent densities. The results are plotted in Fig. 2 on a log-log scale for $s=0.0$ and 0.2 , and $\rho^*=0.28$ and 0.60 .

In the scaling limit, we expect that $R_g \sim N^\nu$, where $\nu = 1/3$ for a collapsed chain, and 0.58 for a swollen chain. All four curves start at $R_g=0.5$ for $N=2$, but the curve for $s=0.2$ and $\rho^*=0.60$ quickly diverges from the other three. After $N \approx 15$, the curve becomes linear, and a fit to the last five points yields a scaling exponent of $\nu = 0.32 \pm 0.01$, implying that the chain is in a collapsed state. This is consistent with the results of Fig. 1. The other curve at $s=0.2$ at the lower density $\rho^*=0.28$ scales more rapidly with N : a fit to the last four points gives $\nu = 0.53 \pm 0.2$, somewhat less than the value expected in the good solvent case. This is also consistent with the results of Fig. 1, which shows this state to be intermediate between the swollen and collapsed state. The two curves at both densities for chains with additive potentials ($s=0$) also scale with N in a manner close to the good solvent prediction: a fit to the last four points of the data yields scaling exponents of $\nu = 0.62 \pm 0.2$ for $\rho^*=0.28$, and $\nu = 0.61 \pm 0.03$ for $\rho^*=0.60$. The fact that the scaling exponents are slightly larger than the good solvent prediction of $\nu = 0.58$ is likely due to the fact that N is very close to, though not yet in, the scaling regime.

In order to gain further insight into the behavior of this system, we analyze the simulation data using a theory developed by Edwards and Muthukumar which predicts the conformational behavior of a Gaussian chain in a random athermal medium of quenched obstacles [7]. It has been argued that for sufficiently large systems the statistical behavior of this system should be identical to that of a chain in a medium

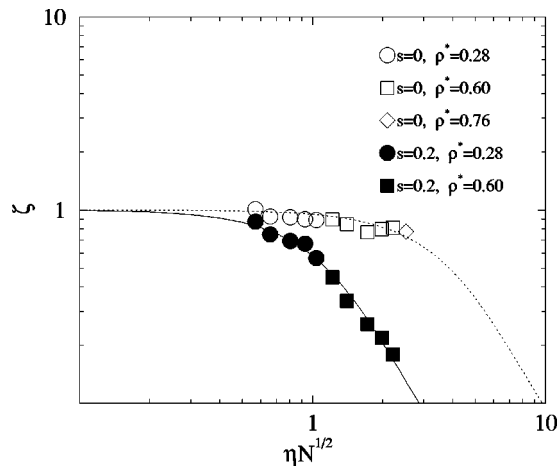


FIG. 3. Comparison of simulation results for the scaled mean-square radius of gyration, $\zeta \equiv R_g^2/R_{g,0}^2$, vs $\eta N^{0.5}$ and the predictions of the theory of Edwards and Muthukumar for a polymer chain immersed in a medium of quenched obstacles. $R_{g,0}^2$ is the mean-square radius of gyration for an isolated chain, and $\eta = (\pi/6)\rho^* = (\pi/6)N_s\sigma^3/V$ is the packing fraction of the solvent. The solid and dashed lines are the fits to the data using Eq. (1) for the nonadditive ($s=0.2$) and additive ($s=0$) cases, respectively.

of annealed obstacles [8,9], and, therefore, that the theory should also be applicable to a chain-solvent system [6]. The theory predicts the following scaling of R_g :

$$\zeta \equiv R_g^2/R_{g,0}^2 = z^{-1}[1 - \exp(-z)], \quad (1)$$

where $R_{g,0}^2$ is the mean-square radius of gyration for an isolated chain, $z = N\eta^2/C$, where η is the packing fraction of the solvent and C is a constant proportional to u^{-2} , where u is a pseudopotential related to the polymer-solvent excluded volume interaction. Figure 3 shows two fits of the simulation data to Eq. (1) using C as an adjustable parameter for the additive ($s=0$) and nonadditive ($s=0.2$) cases.

We find $C=0.83$ from the fit to the data for $s=0.2$, and $C=9.4$ for $s=0$. The latter is likely to be a poor estimate of C due to the lack of data in the large z limit, but the basic result is clear: C is significantly smaller in the nonadditive case since the pseudopotential u describing the solvent-monomer interaction is larger when the excluded volume of the two species is larger. Note that the data for the additive potential systems fall along the flat part of the curve, indicating that they lie in the good solvent regime, consistent with the interpretation of the results of Figs. 1 and 2. By contrast, the data for $s=0$ and $\rho^*=0.60$ lie in the asymptotic regime of $\zeta \sim z^{-1}$ as $z \rightarrow \infty$, the poor solvent scaling prediction, also consistent with the interpretation of the results in Figs. 1 and 2. Further, we note that the data for the nonadditive, low-density system ($s=0.2$, $\rho^*=0.2$) lie in the transition regime between the two limits, also consistent with the intermediate scaling behavior of $\nu=0.53$ discussed above. Based on the theory, we expect that the scaling exponent should approach the poor solvent limit for sufficiently large chains.

In summary, we have studied a polymer in a monomeric solvent interacting with a steeply repulsive interaction, and demonstrated that the chain undergoes an entropy-driven collapse transition when a small degree of nonadditivity is incorporated into the monomer-solvent interaction. The degree of nonadditivity required to induce chain collapse decreases when the density of the solvent increases. This is an entropy-driven collapse transition observed in continuous space for a system where the solvent particles are not significantly bigger than the monomers.

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