POLYMER CHAIN COLLAPSE IN SUPERCRITICAL FLUIDS

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Abstract Recent computer simulations of a polymer chain in a solvent have provided evidence, for the first time, of polymer chain collapse near the lower critical solution temperature (LCST). Motivated by these results, we have studied further this system to understand the effect of solvent and monomer sizes, chain length, and solvent and monomer energetic interactions. By means of extensive Monte Carlo simulations, the mean radius of gyration $R_g$ and end-to-end distance $R$, are calculated for a single chain in a solvent over a broad range of volume fractions, pressures and temperatures. Our results indicate that in general, the chain collapses as temperature increases at constant pressure, or as density decreases at constant temperature. A minimum in $R_g$ and $R$ occurs near the LCST and slightly above the coil-to-globule transition temperature (C-GTT), where the chain adopts a quasi-ideal conformation, defined by the balance of binary attractive and repulsive interactions. At temperatures well above the LCST, the chain expands again suggesting an upper critical solution temperature (UCST) phase boundary above the LCST forming a closed-immiscibility loop. However, this observation strongly depends on the solvent-to-monomer size ratio.

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1. Introduction

As it is well known, polymer solutions also exhibit lower critical solution temperature (LCST) or thermally induced phase separation when temperature is raised. LCSTs have been observed in strongly interacting polar mixtures, for example aqueous solutions, as well as in weakly interacting non-polar polymer solutions. An LCST may also be produced by the mixture’s finite compressibility. Unlike the upper critical solution temperature (UCST), which is driven by unfavorable energetics, a thermodynamics analysis shows that LCST is an entropically driven phase separation.

LCSTs usually occur in the vicinity of the vapor-liquid critical temperature of the pure solvent. Specifically, they are typically observed at about $0.7T^*_c$ to $0.9T^*_c$. Of particular relevance is the phase behavior of polymer solutions in supercritical fluids (SCFs), since most of these systems exhibit an LCST.

The development of a fundamental understanding of the phase behavior of polymer solutions in SCFs is a theoretical challenge of great practical interest[1]. The solution behavior is complex due to large values of free volume, isothermal compressibility, volume expansivity and concentration fluctuations. Practical SCF applications involving LCST phase behavior include polymer fractionation, impregnation and purification, polymer extrusion and foaming, formation of materials by rapid expansion from supercritical solution and precipitation with a compressed fluid antisolvent, dispersion as well as emulsion polymerization, and formation of emulsions and microemulsions [2,3].

It was conjectured some time ago that chain collapse should also be observed near an LCST in an analogous way as it occurs near an UCST [4]. The implications of this polymer physics problem are of great relevance to SCF technology. In 1997, Luna-Bárcenas, et. al. [5], reported for the first time, from extensive numerical calculations, evidence of polymer chain collapse near the LCST upon heating the polymer solution at constant pressure. By investigating single chain architecture, the phase behavior of more concentrated polymer solutions was predicted. In other words, the physics of chain collapse near LCST captures the macroscopic phase separation behavior in a finite concentration polymer solution. Luna-Bárcenas, et. al. observed that the collapse of a single polymer chain correlates well with coil-globule transition temperature (CGT-T) and an occurrence of an LCST phase boundary. It was also observed that upon further heating the collapsed chain expanded.
again suggesting the presence of a closed immiscibility loop. Later, this closed loop was corroborated by direct phase separation simulations using an expanded Gibbs ensemble formalism [5]. However, the above studies were restricted to a fixed chain length, energetic interactions and solvent to monomer size ratio. Motivated by these findings, in this work we report some results of more extensive numerical simulations by investigating the effect, that energetic interactions and monomer to solvent size, have on the phase diagram of a mixture.

2. Molecular model

The system studied in this work consists of a single freely jointed chain immersed in a solvent medium and is analogous to the infinite dilute regime of a polymer system. This regime consists of a polymer system in which chains are far from each other to avoid interchain interactions, that is, the chains act as individual entities. To simulate the intermolecular interactions we used the typical Lennard-Jones (LJ) potential that is defined as,

\[
U_{i,j}(r) = \begin{cases} 
4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] + 0.01632\epsilon_{ij}, & \text{if } r \leq 2.5\sigma_{ij} \\
0, & \text{otherwise}
\end{cases}
\]

In this equation \( r \) is the distance between molecules, \( \sigma_{ij} \) and \( \epsilon_{ij} \) represent the parameters of the potential. Since we have introduced a cutoff of 2.5\( \sigma \) in the interaction LJ potential, it is equal to zero for larger distances. This is equivalent to an upwards shift in the entire potential. The phase and critical behavior of this LJ model have been studied by Smit [6] who reported a reduced critical temperature \( T^* = (K_B T_c/\epsilon) = 1.08 \), a reduced critical density \( \rho^* = \sigma^3 \rho_c = 0.31 \), and a reduced critical pressure \( P^* = P_c \sigma^3/\epsilon = 0.10 \). In this paper, we report results corresponding to a constant chain length of \( N = 20 \) segments or monomers. The strength of the energetic interactions has been varied by changing systematically the ratio \( \epsilon_{11}/\epsilon_{22} \). Here, the subscript 11 refers to the nonbonded monomer-monomer interaction while the subscript 22 is related to the solvent-solvent interaction. In the same manner, the monomer-solvent size effect is considered by varying the ratio \( \sigma_{11}/\sigma_{22} \), with \( \sigma_{11} \) the monomer size and \( \sigma_{22} \) the solvent size. The way the site density is usually defined, \( (\rho^* = \sigma^3 \rho) \) is not appropriate when dealing with objects of dissimilar sizes. Instead, we use the volume fraction, \( \eta = \text{(site volume)}/\text{(total volume)} \) as a more natural variable since it takes into account the volume of the objects, whereas the site density does not.

To study the polymer chain collapse we used the continuum configurational bias (CCB) Monte Carlo algorithm. This method consists in
cutting the chain at a random site. A portion of the chain is then deleted from this site to one of the ends of the chain. Finally, the chain is re-
grown site by site until its original length is restored. A more detailed
description and explanation of this algorithm is presented in reference
[7].

3. Results and discussion

3.1 Solvent-to monomer size ratio effect: (small solvent-big monomer)

To understand better the effect of the monomer-to-solvent size ratio on
the mixture’s phase behavior, we considered a monomer segment volume
that is twice the solvent volume. This is equivalent to consider a ratio
\( \sigma_{11}/\sigma_{22} = 1.26 \), The energetic interactions were chosen such that the
interactions between monomer-monomer and solvent-solvent are equal,
that is, \( \epsilon_{11}/\epsilon_{22} = 1 \) keeping this ratio constant. Figure 1 shows the
mean square end-to-end distance \( < R^2 > \) of the chain as a function of
the system volume fraction at several reduced temperatures, that were
chosen in the vicinity of the pure solvent critical temperature \( T^*_c = 1.08 \).
For reasons of comparison it is important to note that in figure 1 the data labeled with the legend "BASE" represent the results for a symmetric mixture, that is, $\epsilon_{11}/\epsilon_{22} = 1$ and $\sigma_{11}/\sigma_{22} = 1$, as reported in reference [5]. At high densities, the chain adopts a coil-like conformation that approaches the athermal or infinite temperature limit. The chain collapse at low densities suggest that solvent quality diminishes as the solvent density or volume fraction decreases. This behavior is experimentally observed in a pure supercritical fluid. For instance, the square of the solubility parameter (cohesive energy density per unit volume) decreases when the density also decreases. It is interesting to note that going from low to high volume fraction the small solvent-big polymer mixture expands more rapidly than the symetric mixture at fixed temperature. This suggest that a smaller solvent with similar energetic interactions compared to a bigger one acts as a better solvent since the chain is more solvated. Also note from Figure 1 that the increase in chain dimensions with temperature at constant volume fraction –pressure must also increase to maintain constant the density– is consistent with the idea that attractive energetics become less important at high temperatures, that is, $\epsilon/(k_B T) \to 0$. When the chain collapses to enhance favorable intra-
Chain attractive interactions, it does so at the expense of losing chain conformational entropy. Chain connectivity brings chain segments into close proximity to one another—the so called correlation hole—enhancing the effects of intrachain forces relative to chain-solvent interactions. The remarkable behavior of chain collapse with temperature is shown in figure 2. At constant pressure chain dimensions go through a minimum suggesting that a phase boundary is being approached. It has been shown recently [5] that this minimum represents the LCST of the mixture. However, in our case small solvent-big polymer, the chain’s minimum dimension is bigger than the symmetric case, that is, same size solvent and monomer, which is in agreement with the observation made above from figure 1, that smaller solvent solvates better the chain. The expansion of the chain upon further heating—see figure 2—suggest the existence of a one-phase region. These observations were already pointed out in reference [5]. In fact they demonstrated, by direct simulation of phase equilibria, the existence of a closed immiscibility loop in the polymer solvent phase diagram.

Figure 3. Mean square end-to-end distance versus temperature for a big solvent-small polymer system. See text for an interpretation of this figure.
3.2 Solvent-to-monomer size ratio effect (big solvent small polymer case)

In contrast to the previous subsection, we now consider the effect of a solvent that has twice the volume of the monomer unit in the chain, that is $\sigma_{11}/\sigma_{22} = 0.794$. In figure 3 we show the behavior of the mean square end-to-end distance as a function of temperature. It is worth noticing that at a given temperature and pressure, but at temperatures near the solvent’s critical point, the chain collapses when compared to the small solvent-big polymer case. This fact would imply that the mixture would be phase separated until high enough temperatures are reached at which the mixture will again be miscible. The predicted phase behavior is shown in figure 4 on a P-T plane. Figure 4 also shows the effect of different energetic interactions. Two cases are considered: $\epsilon_{11}/\epsilon_{22} = 1.2$ and $\epsilon_{11}/\epsilon_{22} = 1.5$. In both cases, the non-bonded monomer-monomer energetic interactions are stronger than the solvent-solvent and monomer-solvent interactions. These conditions mimic a worse solvent case with respect to the symmetric mixture.

Finally, a few words on the polymer solution phase diagram. The collapsing chain –emulating the infinite dilution– signals the occurrence
of an LCST phase boundary in a more concentrated (finite) solution. Further heating favors the expanding of the chain, which also indicates the existence of a nonhomogeneous region. The macroscopic picture of the above structural changes –collapsing-expanding– of the chain results in a closed immiscibility loop of varying size and shape. For instance, the small solvent-big polymer case predicts a smaller immiscibility region whereas the big solvent-small polymer case predicts a bigger immiscibility window. For illustrative purposes, the expected phase diagram for the different cases explained above is depicted in figure 5.

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