Polymer Chain Collapse in Supercritical Fluids.
1. Molecular Simulation Results

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Summary: A few years ago we reported the first observation, by computer simulations, of polymer chain collapse near the lower critical solution temperature (LCST).[1] In the present work, we extended the above study to understand the underlying physics of a single polymer chain collapse near LCST and its relationship to phase boundaries in the *T-x* plane. Effects of solvent and monomer sizes, and solvent and monomer energetic interactions are studied. Using Monte Carlo simulations, the mean end-to-end distance (R) and gyration radius (R_g) are calculated for a single chain in a supercritical fluid solvent over a broad range of densities, pressures and temperatures. In general, the chain collapses as temperature increases at constant pressure. Upon a further temperature increase, the chain expands again to approach the athermal limit provided that the temperature is sufficiently high. The collapse is related to an LCST phase boundary while the expansion represents the signature of an upper-critical solution temperature (UCST) suggesting the existence of a closed-immiscibility loop. By manipulating the strength of the energetic interactions as well as the solvent-to-monomer size ratio, the size of the size of the immiscibility loop can be fine-tuned. The relationship among size and the segment-solvent energetic interaction are correlated by a conformational parameter (Ψ) for the first time. By monitoring the Ψ behavior, it is possible to predict solution's phase behavior, transition zone from LCST-UCST in a closed-loop miscibility behavior. The above relationship between chain conformation to phase boundaries may be useful in understanding phase stability in compressible polymer-solvent mixtures.

Keywords: Monte Carlo simulation; phase stability; polymer chain collapse

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Introduction

In 1997, we reported for the first time by computer simulation, the collapse of a single chain near a lower critical temperature (LCST) boundary in a dilute polymer-solution.[1] It was observed that upon heating, at constant pressure, the chain collapses near the LCST in an analogous manner as it does when the solution is cooled to approach an upper-critical solution temperature (UCST). However, upon further heating the chain expands again to mediate the chain attractive interactions. This remarkable behavior was related to the existence of a closed-immiscibility window in the phase diagram, in which

an UCST occurred above an LCST phase boundary.[2] de Gennes,[3,4] using scaling arguments, previously observed the *expansion-collapse-expansion* of a polymer chain in a mixture of two solvents near the mixture's critical point. In 1993 Jannink and co-workers showed similar results; however, their treatment does not allow for the case of a polymer dissolved in a single solvent. It is possible that in a mixture of two solvents, one of them could *preferentially* mediate the forces involved in the collapse phenomena, thus precluding the understanding on the effect of a single, compressible solvent on polymer conformation near LCST. Recently Vasilevskaya, et al.,[5,6] using integral equation theory and Monte Carlo simulations obtained similar results. In 1999 Dua and Cherayil[7] reported the first analytical study on polymer conformation near the solvent's critical point. They observed that for conditions away from the critical point the chain is expanded; the chain collapses when approaching the critical point and expands again at the critical point itself. However, none of these studies attempted to relate chain conformation to phase boundaries.

Recently Lizal and Nezbeda[8] showed an NVT ensemble simulation on amphiphilic chains, i.e. repulsive and attractive segment within a chain in a supercritical fluid solvent. Results are similar to those obtained by Luna-Barcenas[1,2] by obtaining a closed-loop miscibility region. Sumi and Sekino[9] showed that solvophilic and solvophobic chains are expanded near solvent's critical point by a cooperative effect among segments and solvents and solvent's density fluctuations.

Li and Hall[10] studied by molecular dynamics the effect of energetic's strength in a solvent-homopolymer system. This was achieved by manipulating segment-segment and segment-solvent (ε^*_{PP}) and segment-solvent (ε^*_{PS}) strengths.

The above observations are in agreement to some recent experimental studies.[11–14] A fundamental understanding on solution's phase behavior and chain conformation is of scientific and technological relevance in the synthesis and processing of polymers by supercritical fluids.[15–25] We now give a brief introduction on the phase behavior and chain conformation of a polymer solution that exhibits both UCST and LCST phase boundaries. This introductory part will serve as the basis for our discussion on chain collapse and its relation to and LCST.

In general, it is known that polymer solutions demix, i.e. to form two-phase systems, upon either decreasing temperature or increasing temperature or both. To a first approximation, low-temperature demixing is driven by enthalpy-related molecular forces, and it is known as the upper critical solution temperature (UCST). Enthalpy-related forces, such as hydrogen bonding can also influence high-temperature demixing. However, such demixing can also be driven by the difference in thermal expansion, and hence the density, between the solvent and polymer. This effect, often referred to as the "free-volume" effect, becomes dominant near and above the solvent critical point, where the solvent density starts decreasing rapidly with increasing temperature (or reducing pressure). This high temperature limit of the one-phase region is known as the lower critical solution temperature (LCST). LCSTs are experimentally observed at about 0.7-1.2 of the critical temperature of the pure solvent. LCST phase behavior is then dominated by the highly compressible nature of the solvent, which in general, tends to make the polymer solution less thermodynamically stable.[1]

At a very dilute polymer concentration and high enough temperatures, but still in the one phase region, polymer molecules adopt their maximum expansion and its gyration radius (R_g) varies approximately as $N^{3/5}$, where N is polymer size. Here the binary energetic interactions among monomers in a long polymer chain are repulsive and the chain tends to expand. We define a very dilute polymer solution as the one in which isolated polymer chains do not see

each other so there is no net interaction among them. As this dilute solution is cooled, the average size of an isolated chain decreases until the θ temperature is reached, and R_g is found to vary as $N^{1/2}$. The θ temperature of a binary polymer-solvent mixture is defined as the limiting upper critical solution temperature for a polymer of infinite molecular weight. At temperatures below the θ temperature solvent is partially expelled from within the polymer coil and the polymer begins to contract and to adopt configurations much smaller than those at the θ temperature. If cooling is continued the interactions become attractive and the polymer chain fully collapses into a globular conformation such that R_g varies as $N^{1/3}$. This phenomenon represents the phase separation of the isolated polymer chain and it is known as the *coil-to-globule* transition (CGT).

In a non-dilute solution, where on average chains overlap with one another, chains adopt an expanded coil-like conformation above and below the θ temperature. However, below the θ temperature, the non-dilute solution can phase split into a phase rich in polymer and into another phase depleted in polymer. A large number of theoretical and experimental studies on the CGT have appeared in the literature and traditionally have been associated with lowering temperature to approach an UCST phase boundary in dilute solutions.[26–34]

In 1979 Sanchez[35] was the first one to conjecture that a chain should collapse when approaching an LCST phase boundary in an analogous manner when approaching the UCST. In 1997 our group reported the first evidence of chain collapse near LCST by computer simulation.[1] However this study focused only in *symmetric* Lennard-Jones polymer-solvent mixtures in which the polymer chain size was kept constant. The system is symmetric in that solvent and a polymer segment are identical, i.e. the monomer-to-solvent ratios for the energetic interactions and sizes were kept constant to 1.0, respectively. The Flory "chi" parameter χ is propor-

tional to $\varepsilon_{11}+\varepsilon_{22}-2\varepsilon_{12}$, in which the ε's represent the "strength" of the attractive interactions. For symmetric mixtures, χ is exactly zero. In this context, such a symmetric mixture is not likely to phase separate in the low temperature limit (UCST). However when the dilute polymer mixture was taken near the critical point of the pure solvent (large density fluctuations), the polymer chain collapsed from an expanded state and upon further temperature increase the chain expanded again. Remarkably, we also showed that when the isolated chain crossed the CGT temperature (upon heating at constant pressure) it represented the direct signature of the occurrence of an LCST phase boundary for the non-dilute solution.[2] For higher pressures, the solvent mediates the attractive monomer-monomer interactions (good solvent) such that the chain collapses to a lower extend. For high enough pressures the chain remains relatively unperturbed from its vacuum dimensions upon heating.[27] This case represents the limiting pressure in which the two-phase region vanishes and the system becomes fully miscible. In the future it would be interesting to study the effect of size and energetic differences and their effect on the shape of the phase diagram.

The above observations can be analyzed in terms of the phase stability near the vapor-liquid critical point of the solvent by invoking the isothermal stability condition: $(\partial^2 g/\partial\phi^2)_P = (\partial^2 a/\partial\phi^2)_\rho - \beta/\rho(\partial P/\partial\phi)^2_\rho > 0$, where g and a are the intensive Gibbs and Helmholtz free energies (per monomer of solution), β is the isothermal compressibility of the solution, ρ is the solution monomer density and ϕ is the occupied volume fraction of either component. The first term of the right-hand side is the "incompressible contribution" and is expected to be positive for symmetrical energetics. The second term, the "compressible contribution", is scaled by the solution compressibility and always contributes unfavorably to phase stability since β increases as the critical point is approached (β diverges to infinity at the

critical point). In an infinite dilute polymer solution, the solvent properties dominate as the vapor-liquid critical point is approached and the solution becomes unstable and phase separates into two fluid phases. Thus, it is clear that finite compressibility and equation of state differences among components play an important role in solution phase behavior.

Polymer-supercritical fluid solution behavior is complex due large values of free volume, isothermal compressibility and concentration fluctuations. Practical SCF applications involving LCST phase behavior include formation of particles,[18,21] stabilization of latexes,[19] polymer fractionation[15,36] and impregnation and dyeing.[37] Also many polymers and copolymers have been synthesized in supercritical carbon dioxide by means of homogeneous, precipitation, dispersion, emulsion and suspension polymerization schemes.[18,38,39]

One of the most used SCFs is CO_2 since it is nontoxic, nonflammable and relatively inexpensive, it also has a relatively low critical point (32 °C, 74 bar); it represents as viable substitute of volatile organic solvents. SCF CO_2 is an excellent polymer plasticizer, thus it facilitates impregnation with dyes or drugs for delivery systems.[40] The group of Keith Johnston (U. Texas) related the solubility of a polymer in supercritical CO_2 to the surface tension of the pure polymer.[41] Surface tension is directly related to the cohesive energy density of the polymer and consequently it is a measure of the polymer-polymer interactions. Low surface tension polymers, such as fluorine and silicon based polymers show appreciable solubility in SCF CO_2. However most commercial polymers, such as polystyrene, poly(methyl methacrylate) or polyethylene are practically insoluble in SCF CO_2 up to 200 °C and 2000 bar.[42] To overcome the solubility limitation, dispersion polymerization in SCF CO_2 schemes have been utilized in the production of polymethacrylates, polyacrylates and polystyrene.[43] Dispersion polymerizations require the use of a polymeric surfactant

to sterically stabilize polymer particles to avoid their flocculation and precipitation. The solvation of the stabilizing chains by the SCF medium must be sufficient to mediate polymer-polymer interactions otherwise solvent will be expelled from the chains producing flocculation.[44] Recently coil-to-globule transition (CGT) studies were extended to understand the stability of colloids in a Lennard-Jones SCF, by Monte Carlo simulation, by a block copolymer as stabilizer.[45] It was observed that upon an isothermal decrease in density (or pressure) colloidal flocculation occurred at a critical value, so-called critical flocculation density (CFD). This CFD coincided with the coil-to-globule transition (CGT) density (or pressure) on the bulk phase diagram where the stabilizer chains collapse in the solvent.[46] The collapse of grafted chains precedes flocculation and phase separation of the particles, just as collapse and phase separation occur in bulk solutions. Unfortunately both bulk[1] and colloidal[44] phase behavior studies have focused only in symmetric Lennard-Jones systems where the properties of polymer segments match those of the solvent.

The overall objective of this work is to understand the underlying physics of polymer chain collapse near LCST, by computer simulation, and to relate it to phase boundaries in the *T-x* plane. We also attempt to provide a more comprehensive molecular-based description of the collapse by studying the effect of solvent and monomer sizes, and solvent-to-monomer energetic interactions.

Simulation Details

The systems studied in this work consist of a single freely jointed chain immersed in a solvent medium. This mixture is analogous to the infinite dilute regime, such that polymer chains are far from each other to avoid interchain interaction. In other words, a single chain is isolated from others and it acts as an individual entity. The

typical Lennard-Jones (LJ) potential is used to simulate the energetic interactions, and is given by

$$U_{ij}(r)$$
$$= \begin{cases} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + 0.01632\varepsilon_{ij} & r \geq 2.5\sigma_{ij} \\ 0 & r < 2.5\sigma_{ij} \end{cases}$$
$$(1)$$

where r is the site-site distance, and where σ and ε are potential energy function parameters. The LJ potential only operates to distances up to 2.5σ (the cutoff); for larger separations the potential is assumed to be zero, i.e. the entire potential is shifted upward. Three types of interactions are considered: non-bonded segment-segment, segment-solvent and solvent-solvent interactions.

The phase and critical behavior of this LJ model has been reported by Smit[47] with values of critical temperature, $T_c^* = kT_c/\varepsilon = 1.08$, reduced critical density, $\rho_c^* = \sigma^3\rho_c = 0.31$, and a reduced critical pressure, $P_c^* = P_c\,\sigma^3/\varepsilon = 0.10$.

In this work, the continuum configurational bias (CCB) Monte Carlo method was used to perform polymer chain movements. The method consists in cutting the chain at some random site. A portion of the chain is deleted from this point to one of the ends. The chain is regrown site by site until its original length is restored. Details on the computer implementation of the CCB method and its capabilities and limitations have been discussed elsewhere.[48,49]

The above CCB method is then applied in a canonical (*NVT*) ensemble formalism. There are three independent variables to be specified: system temperature, T^*, density, $\rho^* = \sigma 3\rho$ and the number of molecules. In this work, T^* is varied from 1.1 to 5.0 and ρ^* from 0.0 to 0.5 and number of solvent particles from 0 to about 3000 for $0 < \rho^* < 0.5$. Relaxation of the solvent was achieved by random displacement Monte Carlo moves. The chain length is varied for $N = 20$, 30 and 40 segments. Statistics for conformational properties such as the mean square end-to-end distance $\langle R^2 \rangle$ and the mean square radius of gyration $\langle R_g^2 \rangle$ were

Table 1.
Summary of conditions studied in this work.

Effect of:	$\varepsilon_{mm}/\varepsilon_{ss}$	σ_{mm}/σ_{ss}*
Energetics	0.6	1.00 (1/1)
	1.2	1.00 (1/1)
	1.5	1.00 (1/1)
	2.11	1.00 (1/1)
Size	1.0	1.26 (2/1)
	1.0	1.71 (5/1)
	1.0	0.79 (1/2)
	1.0	0.58 (1/5)
Energetics and size	0.6	0.844 (0.6/1)
	1.5	1.145 (1.5/1)
	1.5	1.26 (2/1)
	2.0	1.26 (2/1)
	1.2	0.79 (1/2)

*Numbers in parenthesis denote the monomer-to-solvent volume ratio (V_m/V_s).

collected for $O(10^7)$ steps after an equilibration period of $O(10^6)$. This strategy gives $O(10^6)$ successful chain moves.

The strength of the energetic interactions is varied by manipulating the $\varepsilon_{mm}/\varepsilon_{ss}$ ratio, where ε_{mm} represents the non-bonded monomer-monomer interaction and ε_{ss} is the solvent-solvent interaction. For monomer-solvent interactions, ε_{ms} and σ_{ms}, the Lorenz-Berthelot mixing rules are used. Size effects are characterized by varying the σ_{mm}/σ_{ss} ratio, where σ_{mm} is the monomer segment size and σ_{ss} the solvent segment size. Table 1 summarizes the conditions studied in this work.

Results and Discussion

Chain Dimensions in Vacuum

Figure 1 shows typical behavior of an isolated chain in vacuum for a chain size $N = 20$-40. By manipulating its temperature, $T^* = kT/\varepsilon$, the solvent quality is emulated. In such systems the strength of the attractive interactions is proportional to ε/kT, i.e. at high enough temperatures the chain expands and at low temperatures the chain collapses (good-to-poor solvent regime transition).[35] Note that the curves for different molecular weights intersect at a unique temperature. This temperature is defined as the coil-to-globule temperature (C-GTT) in vacuum; for an infinite molecular weight polymer C-GTT becomes the θ
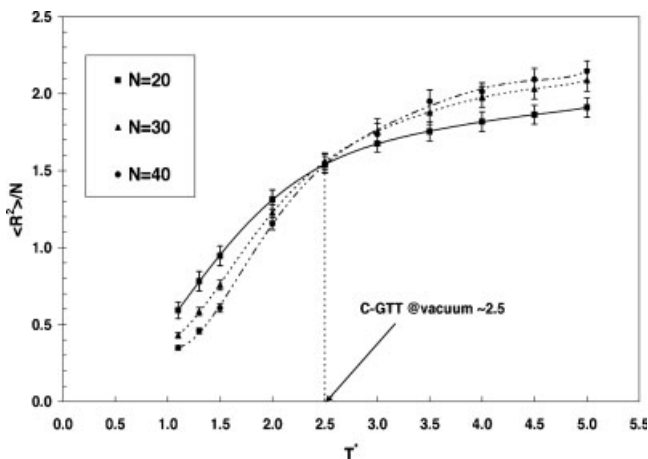
Figure 1.
Normalized square end-to-end distance as a function of reduced temperature T^* in vacuum.

temperature. At θ attractive and repulsive forces compensate and the chain behaves *quasi-ideally*.[50]

For our system C-GTT is about 2.5. This value is of great importance since it divides two regions in a dilute polymer solution: above θ the polymer adopts coil-like conformations (good solvent), whereas below θ the polymer will begin to collapse. Also, above θ large fluctuations in chain dimensions occur whereas small fluctuations are expected below θ.[51]

In vacuum, the dimensions of an isolated polymer chain are determined by two opposing forces: intrachain attractive forces act to collapse the chain to a compact, globular form and entropic forces act to keep the chain expanded in random coil-like conformations. Upon cooling a coil-to-globule transition occurs at a unique temperature (C-GTT) for an infinite chain where intrachain attractive forces overcome the entropic force. From Figure 1, the C-GTT in vacuum is about 2.5. It is noteworthy that the 2.5 value depends on the specific potential used (see Equation 1). Consequently, it is important to characterize the C-GTT in vacuum for our model system.

Effect of Energetics on Chain Dimensions
To isolate the effect of energetic interactions on chain dimensions the $\varepsilon_{mm}/\varepsilon_{ss}$ ratio

is manipulated while keeping the size ratio σ_{mm}/σ_{ss} constant (see Table 1 for full details). Figure 2 shows the mean square end-to-end distance $<R^2>$ of the chain as a function of the system density at several reduced temperatures. Two cases are studied for a chain length $N=20$: $\varepsilon_{mm}/\varepsilon_{ss}=1.2$ and 1.5 ($\sigma_{mm}/\sigma_{ss}=1.0$ for both cases). The data labeled *symmetric* are the results for a polymer-solvent mixture in which $\varepsilon_{mm}/\varepsilon_{ss}=1.0$ and $\sigma_{mm}/\sigma_{ss}=1.0$. In general, at high densities the chain is expanded in a coil-like conformation. Note that along an isotherm, the system pressure varies in the same fashion as the density does, i.e. at constant temperature increasing solvent density requires an increase in pressure. The collapse of the chain at low densities suggests that the solvent quality diminishes as the solvent density decreases. Recent SANS experiments on near-dilute polymer in SCF CO_2 solutions[12,13,52] show a similar behavior as depicted in Figure 2: the polymer starts to collapse as the experimental pressure (or density) of the system decreases at constant temperature. Upon further pressure decrease and approaching the θ temperature (note that there is an corresponding θ pressure) the polymer collapses to adopt its unperturbed dimensions. When the system pressure is further reduced the polymer chain dimensions unexpectedly remain relatively
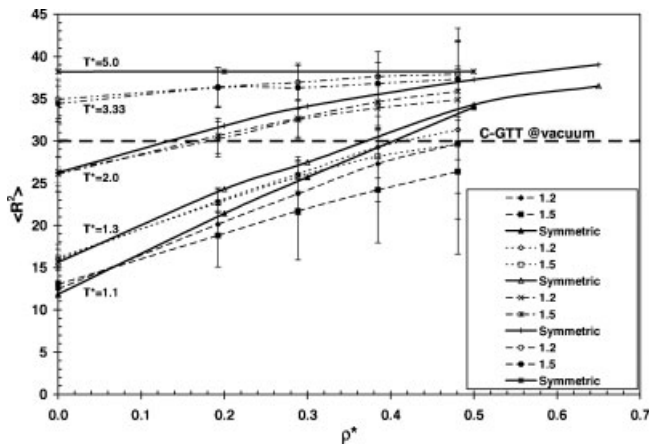
Figure 2.
Mean-squared end-to-end distance as a function of solvent density for two energetics ratios: $\varepsilon_{mm}/\varepsilon_{ss} = 1.2$ and 1.5. Solid lines represent a symmetric mixture in which the properties of the solvent match those of the monomer unit. All lines are only a guide to the eye.

unchanged for the experimental pressure range studied. It is possible that chain overlap precludes further collapse upon depressurization for the near-dilute polymer solutions. In the future it would be interesting to explore chain behavior more fully with experiments that cover wider temperature and pressure ranges. Also lower polymer concentrations are required to avoid interchain interpenetration. The concentration transition C^* which divides the dilute and semi-dilute regimes in a polymer solvent mixture can be used to experimentally determine the proper polymer concentration.[53]

It has been observed that the stability of a latex in a supercritical CO_2 medium decreases as the CO_2 density decreases.[19] In these colloidal systems, one key requirement for stability is that the stabilizing chains must be solvated in the SCF phase, i.e. the chains must extend out into the SCF. The review paper of Johnston[19] covers a great deal of work done in understanding phase equilibria of copolymers used as stabilizers in SCF CO_2. In these studies, as the solvent density was lowered, the colloid flocculated at a critical solution density (CFD) due to a loss of in solvent quality. It was demonstrated, by computer simulation,[46] that CFD coincided with coil-to-

globule transition density of a bulk solution. This elegant analogy between colloid flocculation and bulk phase separation is being proven useful for designing surfactants in SCF technology. However, the above relationship has only been studied for symmetric mixtures, i.e. monomer properties match those of the solvent. From Figure 2 it is expected that an increase in the mismatch of polymer-to-solvent properties will have a strong impact on the system's phase behavior.

In the absence of solvent (vacuum)(see Figure 1), the dimensions of an isolated chain are determined by two opposing forces: intrachain attractive forces tend to keep the chain in a globular state, whereas entropic forces tend to keep the chain expanded. Upon cooling a coil-to-globule transition occurs at a unique temperature (C-GTT) where intrachain attractive forces overcome the entropic force. From Figure 1, C-GTT in vacuum is about 2.5. The primary effect of adding a solvent to a chain in vacuum is to mediate the intrachain attractive forces by a "screening" mechanism.[1] The presence of solvent screens the intrachain attractive interactions by excluding close intrachain contacts. From Figure 2, it is clear that increasing density (or pressure) the solvent effectively

screens the intrachain interactions such that the chain expands. Also note that the chain dimensions are all shifted upward as solvent density increases and the isotherms begin to merge. The merging and rising of the isotherms indicate that the strength of intrachain attractive interactions is being effectively screened by the solvent. For high enough temperatures ($\sim T^* > 5.0$), the chain reaches its maximum dimensions. This observation is consistent with the idea that attractive forces become less important at high temperatures ($\varepsilon/kT \rightarrow 0$) where attractive forces are ineffective (athermal limit).

Regards the effect of segment-solvent interactions one can analyze Figure 3 at $T^* = 2.0$. As the segment-segment interaction varies from $\varepsilon_{mm}/\varepsilon_{ss} = 1.0 \rightarrow 1.2$ ($\sigma_{mm}/\sigma_{ss} = 1.0$), the solvent does not screen segment-segment interactions and thus requiring higher pressures for the chains to solvated. Now if $\varepsilon_{mm}/\varepsilon_{ss}$ varies $1.0 \rightarrow 1.2 \rightarrow 1.5 \rightarrow 2.11$, chains are collapsed for a wider density range. It is expected that even higher densities (pressures) are required to cross the C-GTT line with respect to a symmetric mixture. By increasing the $\varepsilon_{mm}/\varepsilon_{ss}$ value, intrachain attractions are favored, whereas if $\varepsilon_{mm}/\varepsilon_{ss}$ is lower than 1.0, say 0.6, chains are well solvated by the solvent. This observation has been pointed out by Li and Hall[10] where the segment-segment interaction plays an important role in the mixture's phase behavior. However, more studies are required to fully understand phase behavior.

By careful inspection of Figure 2 an interesting trend is observed: at the isotherm $T^* = 1.1$ increasing intrachain forces ($\varepsilon_{mm}/\varepsilon_{ss} \uparrow$) promote stronger collapse of the chain relative to the symmetric case as previously explained. At $T^* = 1.3$ the collapse is somewhat less pronounced than the one seen at $T^* = 1.1$. As the temperature increases, say to $T^* = 2.0$ and 3.33 intrachain forces are screened by thermal energy in such way that the system approaches the athermal limit ($\sim T^* > 5.0$) and the energetic mismatch is less important. In general, intrachain forces are mediated by an increase of density (or pressure) or by an increase in thermal energy promoting expansion of the polymer chain. Figure 2 suggests that any mismatch of monomer-to-solvent energetic interactions may be mediated at *sufficiently* high temperatures or pressures (densities).

Figure 4 shows the full chain behavior with temperature for several isobars. At constant pressure, chain dimensions go through a minimum in analogous way as it does when cooling the system to approach an UCST boundary. In our previous study[1]
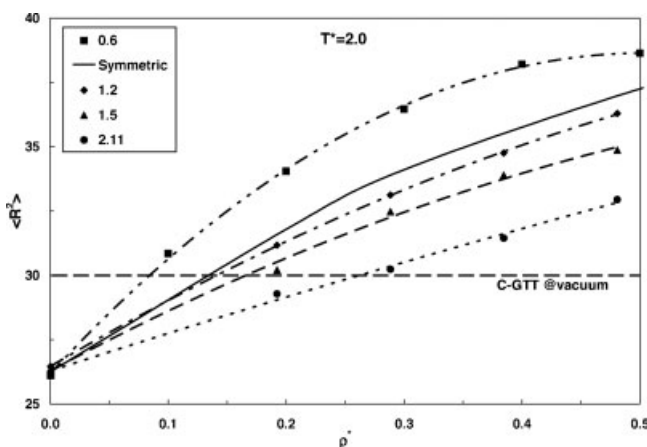

Figure 3.
End-to-end distance as a function of solvent density. Effect of energetic interactions ($\varepsilon_{mm}/\varepsilon_{ss} = 0.6$, 1.0, 1.2, 1.5, 2.11) for $T^* = 2.0$
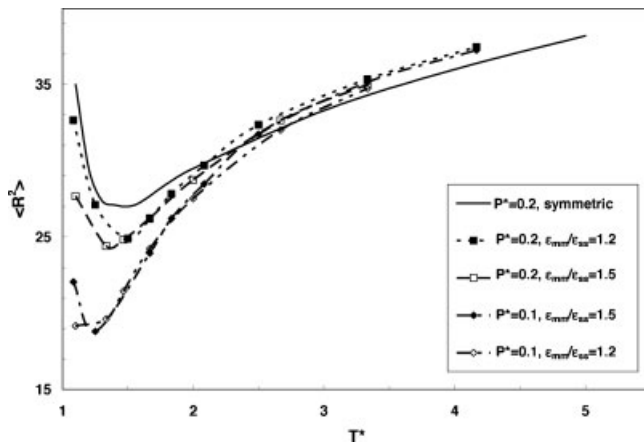
Figure 4.
Mean-squared end-to-end distance as a function of temperature for two pressures, $P^* = 0.1$ and 0.2 ($P^*_c = 0.1$).

we showed, by expanded ensemble simulations of a finite concentration polymer solution, that the temperature and pressure at which the chain collapses most represents the direct signature of an LCST phase boundary. Increasing system's asymmetry ($\varepsilon_{mm}/\varepsilon_{ss} > 1.0$) causes the chain to collapse more. It is expected that a more pronounce collapse will have a strong impact on the LCST behavior. The rest of this paper addresses these issues.

From Figure 4 it is observed that upon heating the chain begins to expand again implying that solvent quality is improving. Note that the density is very low. This expansion is related to a one-phase miscible solution above LCST. In other words, an UCST is encountered above an LCST forming a closed immiscibility loop. Note that when the pressure increases chain collapse is less pronounced. Without much collapse, phase separation is not expected. Also, as P^* is reduced approaching solvent's critical pressure of 0.1, chain collapse is more pronounced. Experimentally LCSTs are observed near the solvent's critical point.[54]

One may conjecture that above results strongly depend on the potential function used in our current and previous studies (see Equation 1). However, In 1999 Dua and Cherayil,[7] using an integral equation treatment in the self-consistent Edwards-Singh limit, reported the first analytical study on polymer conformation near the solvent's critical point. They observed that for conditions away from the critical point the chain is expanded; the chain collapses when approaching the critical point and expands again at the critical point itself. These results are in complete qualitative agreement with our observations suggesting that a simple Lennard-Jones captures the correct physics of chain collapse in a compressible medium. As explained before, recent SANS studies[12,52] show similar results; however, those studies did not show further chain collapse when crossing θ conditions upon depressurization and approaching the solvent's critical point. Concentration effects precluded further collapse due to chain overlap in these semi-dilute polymer solutions. In summary, more experimental studies are needed to attempt correlating chain collapse to both theoretical and simulation predictions.

The parameter $\aleph = <R^2>/6<R^2_g>$ has been used to understand chain's phase behavior by des Cloizeux and Jannink.[50] For an ideal chain $\aleph = 1$, for real chains $\aleph = 1.05$–1.07.[1] Figure 5 shows $\aleph$ as a function of density for different temperatures; for the case of $\varepsilon_{mm}/\varepsilon_{ss} = 1.5$. It is observed that as $\varepsilon_{mm}/\varepsilon_{ss}$ increases higher densities are required to solvate and expand the chains. The crossover value
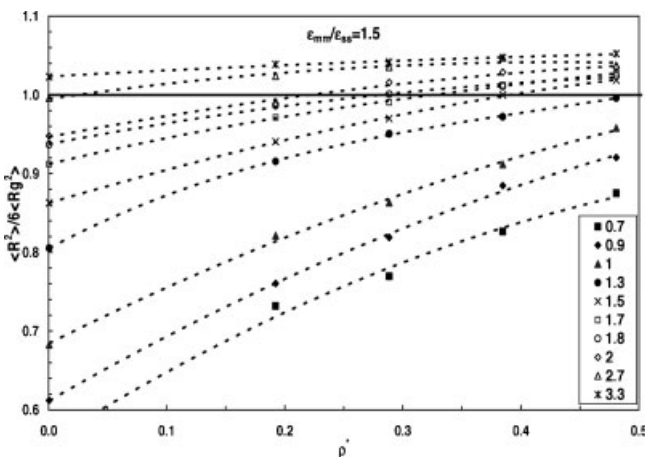
Figure 5.
$\aleph$ behavior as function of solvent's density at different temperatures for $\varepsilon_{mm}/\varepsilon_{ss} = 1.5$.

from collapsed to expanded occurs at $\aleph = 1.0$. In vacuum at $T^* = 2.5$, $\aleph = 1$ which denotes ideal chain behavior.

Figure 6 shows the effect of solvent density on the C-GTT. Note that the primary effect of the solvent is to lower the C-GTT relative to its value in vacuum (≈ 2.5) by the screening mechanism mentioned earlier. The dashed lines represent various isobars for the pure L-J solvent obtained with the Johnson equation of state.[55] Note that some solvent isobars cross the C-GTT curve at two points. We previously showed[1] that the low and high

temperature crossings are associated with an LCST and a UCST which forms a closed-immiscibility loop in the *T-x* plane. When the energetics are varied from $\varepsilon_{mm}/\varepsilon_{ss} = 1.2$ to 2.11 the C-GTT is shifted to higher values with respect to symmetric energetics ($\varepsilon_{mm}/\varepsilon_{ss} = 1.0$). This implies that the LCST is shifted to lower values and the UCST to higher ones to form a *bigger* immiscibility window. When the energetics mismatch between a monomer and a solvent molecule grows the polymer solution will likely be less stable to a temperature increase relative to the symmetric case. Conversely,
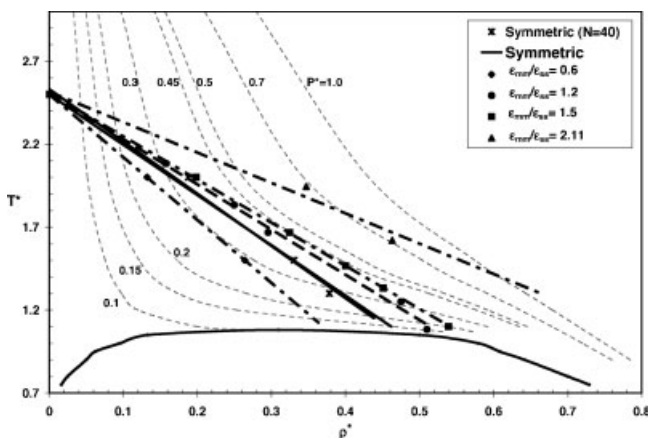

Figure 6.
Coil-to-globule transition temperature (C-GTT) response to solvent density for different segment-to-solvent energetic interactions.

lowering $\varepsilon_{mm}/\varepsilon_{ss}$ values, say to 0.6, polymer miscibility is favored, thus reducing the immiscibility window. If pressure increases for a given $\varepsilon_{mm}/\varepsilon_{ss}$, miscibility increases.

Figure 6 also shows the C-GTT curve for a chain length $N = 40$ with symmetric energetics; it can be observed no differences with respect to a chain length $N = 20$. We also found that the C-GTT curve of varying energetics for $N = 40$ (not shown) is statistically similar to the results reported for $N = 20$. Due to these observations the rest of the paper will only deal with $N = 20$.

It is important to emphasize that there exists a corresponding C-GT pressure (not shown) in an analogous fashion as the C-GTT. The first evidence for a C-GTP was previously reported by our group in 1997.[1] Operationally, the C-GTT and C-GTP should give the temperature-pressure condition for the θ-point in the limit of an infinite molecular weight polymer. On the experimental side, recent SANS work on the phase behavior of a near-dilute polymer-SCF CO_2 mixture have addressed the concept of a θ-pressure.[13,52]

As previously discussed, the collapsing of a single chain in a highly compressible solvent medium represents the direct signature of an LCST phase boundary (@P = constant) and upon a further temperature increase the chain re-expands to form a one miscible phase. In this sense, the

response of the C-GTT and C-GTP to solvent density aids in the construction of a T-x (or P-x) phase diagram for the finite-concentration solution. Figure 7 shows the *predicted T-x* phase diagram, based upon single chain collapse simulations, for a binary polymer-solvent mixture that exhibits both an LCST and a UCST phase boundaries. Note that the size of the immiscibility window proportionally increases with the monomer-to-solvent energetics mismatch.

Effect of solvent-to-monomer Size Ratio

Big Monomer-Small Solvent
To understand better the effect of the monomer-to-solvent size ratio on the mixture's phase behavior, this ratio is set to $\sigma_{mm}/\sigma_{ss} = 1.26$ and 1.71. This implies that a monomer volume is two and fives times bigger than that of the solvent, respectively (see Table 1 for full details of conditions). The energetic interactions were kept constant to $\varepsilon_{mm}/\varepsilon_{ss} = 1.0$. Once again the data labeled *symmetric* represent a symmetric mixture in which $\varepsilon_{mm}/\varepsilon_{ss} = 1.0$ and $\sigma_{mm}/\sigma_{ss} = 1.0$. Figure 8 shows the mean square end-to-end distance $<R^2>$ of a chain that is composed of monomers five times bigger than a solvent molecule ($V_{mm}/V_{ss} = 5$) as a function of the system density. At high densities, the chain adopts expanded
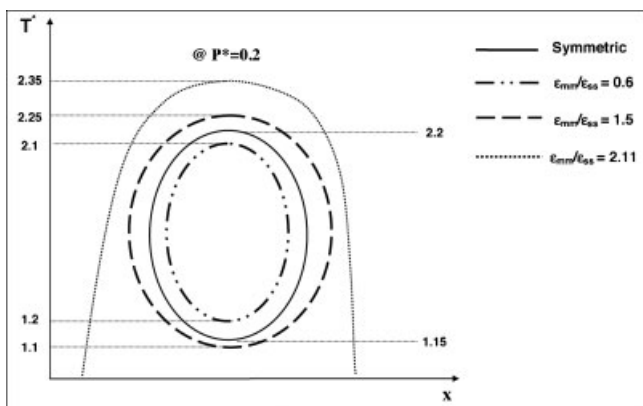

Figure 7.
Temperature-composition phase diagram for a polymer-supercritical solvent mixture "predicted" from single chain collapse studies.
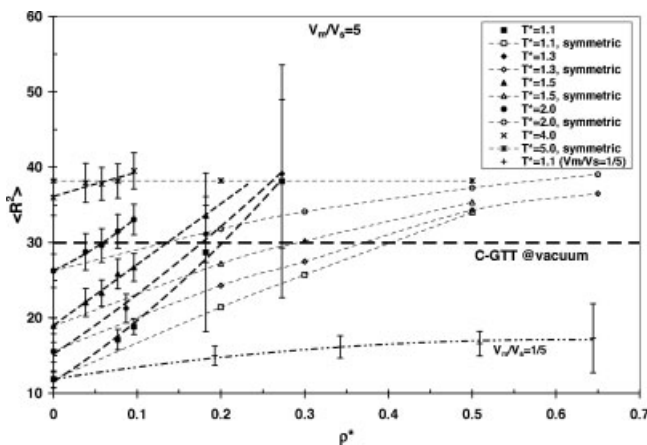
Figure 8.
Mean-squared end-to-end distance as a function of solvent density for a mixture composed of a solvent molecule in which its volume is five times bigger than the monomer unit. Dashed lines denote a symmetric mixture. All lines are shown as a guide to the eye.

coil-like conformations; the chain contraction at low densities (and pressures) suggests that solvent quality diminishes. It is interesting to note that going from low to high density (or pressure) the *big monomer-small solvent* mixture expands more rapidly than the symmetric mixture at a given temperature. These results suggest that a smaller solvent with similar energetic interactions compared to a monomer segment acts as a *better solvent* since the chain is more solvated at a given temperature and density (or pressure) when compared to the symmetric mixture (see Figure 8). Also note from Figure 8 that the increase in chain dimensions with temperature at constant density is again consistent with the idea that attractive energetics become less important at high temperatures. The results (not shown) for a monomer with a volume five times bigger than that of a solvent are similar to those presented above; for a given density and temperature the chain is more expanded, for T^*s ≤ 4.0 with respect to the *smaller* monomer and symmetric cases. Once again, at sufficiently high temperatures all isotherms rise and merge to reach the athermal limit.

Figure 8 also shows the results for a small monomer and a five-time bigger solvent molecule (*small monomer-big solvent case*).

It can be seen that the response of $<R^2>$ to density (or pressure) is completely different to the *big monomer-small solvent* case. Indeed, the chain dimensions remain almost statistically invariant as the system density increases, i.e., chain remains as collapsed as in its vacuum dimensions. In the next section a *small monomer-big solvent* mixture is studied in more detail and its relation to phase boundaries.

Small Monomer-Big Solvent
In contrast to the previous section, we now study the effect of a solvent with a volume two and fives times bigger than that of a monomer segment ($\sigma_{mm}/\sigma_{ss} = 0.79$ and 0.58, respectively). In Figure 9 $<R^2>$ is shown as a function of density for $T^* = 2.0$ for all sizes studied. It is clearly observed that for segments bigger than solvents, chains are more expanded (solvated) when compared to the symmetric mixture. Also note that lower pressures (densities) are required to solvate the chain. Conversely, when the solvent is bigger than the segment, chains are not well solvated and remain collapsed for higher densities (pressures). Note for the case of $V_m/V_s = 1/5$, the C-GTT is not intersected, thus chains are collapsed and consequently a polymer solution would be phase separated.
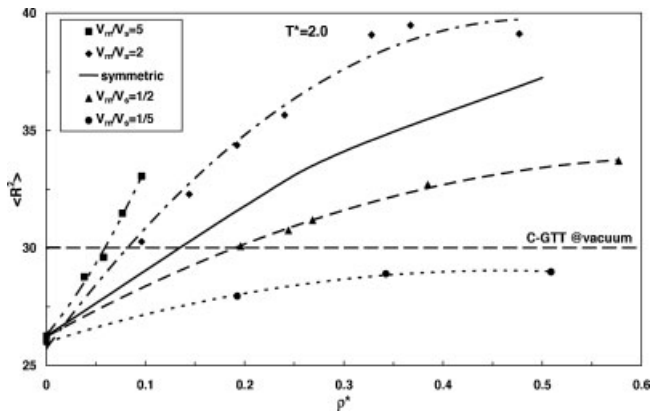
Figure 9.
End-to-end distance behavior for different monomer-to-solvent size (volume) ratios for $T^* = 2.0$.

Chain dimensions as a function of temperature are plotted in Figure 10 for the selected pressure of $P^* = 0.2$ ($P_c^* = 0.1$). For our case in which a monomer unit is smaller than a solvent molecule, it is worth noting that at a given temperature and pressure the chain is more collapsed when compared to the symmetric and *small solvent-big polymer* cases. Note that in Figure 10 the symmetric and *small solvent-big polymer* cases are also shown for comparison. These results suggest that a bigger solvent may act like a worse solvent for the polymer. This fact would imply that the mixture would be phase separated until

high enough temperatures or pressures are reached, in which the mixture will again be miscible. As a consequence of the above, it is expected that immiscible region in the *T-x* will broaden (not shown).

Combined Effect of Size and Energetics
A parameter that can capture the effect of size and energetic simultaneously is the cohesive energy density ξ_i given by[56,57]:

$$\xi_i = \frac{\Delta_{vap} u}{v_i^L} \tag{2}$$

where $\Delta_{vap} u$ is the energy of vaporization and v_i^L is the volume of component *i*. For LJ
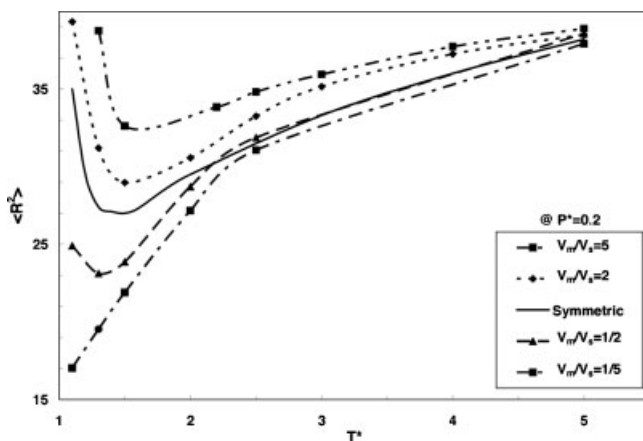

Figure 10.
Mean-squared end-to-end distance of a polymer chain as a function of system temperature for a mixture in which the solvent volume is two- and five-times bigger than the monomer one.

Table 2.
Ψ values for different sizes and energetics.

$\varepsilon_{mm}/\varepsilon_{ss}$	σ_{mm}/σ_{ss}	Ψ	Regime
1	1.71	0.2	**Good solvent**
1	1.26	0.5	
0.6	1	0.6	
1.5	1.26	0.7	
1	1	1.0	**Symmetric (base case)**
0.6	0.844	1.0	**Asymmetric**
1.5	1.145	1.0	**Asymmetric**
2	1.26	1.0	**Asymmetric**
1.2	1	1.2	**Poor solvent**
1.5	1	1.5	
1	0.79	2.0	
2.11	1	2.1	
1.2	0.79	2.4	
1	0.58	5.1	

systems, the cohesive energy density is given by:

$$\psi_i = \frac{\varepsilon_{ii}}{\sigma_{ii}^3} \qquad (3)$$

A conformational parameter can now be defined, Ψ

$$\Psi = \frac{\psi_m}{\psi_s} = \frac{\left(\varepsilon_{mm}/\sigma_{mm}^3\right)}{\left(\varepsilon_{ss}/\sigma_{ss}^3\right)} = \frac{\left(\varepsilon_{mm}/\varepsilon_{ss}\right)}{\left(\sigma_{mm}/\sigma_{ss}\right)^3} \qquad (4)$$

This conformational parameter Ψ can be used to consolidate the effect of size and energetic into a *universal* behavior. Table 2 shows consolidated results for all cases discussed in this study. Figure 11 shows the Ψ–behavior in the C-GTT plane. If Ψ

decreases below 1.0 chains expand (good solvent regime); for $\Psi > 1.0$ chains collapse.

In summary, the conformational parameter Ψ can be used to understand the effects of size and energetic in a consolidated fashion.

Conclusions

In the present study we have attempted to relate conformational changes of a single polymeric chain immersed in a supercritical fluid solvent to phase boundaries in the *T-x* plane. By increasing the mixture's temperature at constant pressure, the chain collapses near the critical temperature of the pure solvent in an analogous fashion as it does when cooling to approach the UCST. A further increase in temperature, the chain expands to reach the athermal limit provided that sufficiently high temperatures are reached. The collapse of the chain signals the occurrence of an LCST phase boundary in a more concentrated (finite) solution. The expansion of the chain as temperature increases suggests the existence of a one-phase region. The macroscopic picture of the above conformational changes (collapsing-expanding chain) are related to the existence of a closed immiscibility loop of varying size and shape which strongly depends on energetics
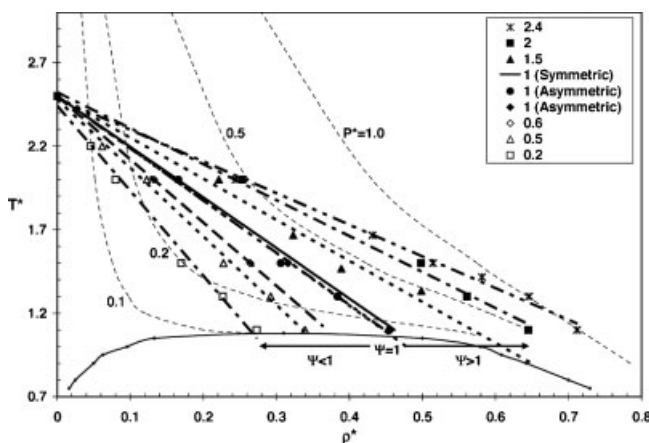
Figure 11.
Effect of Ψ on phase behavior of polymer solution.

and sizes among the polymer chain and the supercritical fluid solvent. For instance, if the energetic mismatch between a mono-mer unit and a solvent molecule increases the immiscibility loop increases. Similarly as the solvent gets bigger compare to a monomer, the solvent acts as a worse solvent and the immiscible region increases. In general, there is a strong interplay among energetics and size effects which ultimately affect chain conformation and phase behavior.

The conformational parameter Ψ can be used to understand the effects of size and energetic in a consolidated fashion.

The above relationship between chain conformation to phase boundaries may be useful in understanding phase stability in compressible polymer-solvent mixtures which is relevant in the formation of latexes, polymer particles with sub-micron features and polymerization reactions.[15–25,58] For instance, to produce a stable colloidal system in a SCF medium the stabilizing chains must be well solvated to mediate polymer-polymer interactions otherwise solvent will be expelled from the chains and flocculation will occur.[44] Any mismatch among the chains and the SCF will tend to promote less solvation that will ultimately lead to a unstable system.

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