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A Unified Understanding of Cononsolvency of Polymers in Binary Solvent Mixtures

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Abstract

Standard Random Phase Approximation (RPA) model are applied to investigate cononsolvency of polymers in mixtures of two good solvents. It is shown that under the RPA framework the two types of cononsolvency behaviors reported in previous theoretical studies can be unified under the same concept of mean-field density correlations. The two types of cononsolvency are distinguished by the solvent composition at which maximum immiscibility are predicted to occur. The maximum immiscibility occurs with the cosolvents being the minor solvent if the driving mechanism is the preferential solvation of polymers. For the cononsolvency driven by the preferential mixing of solvents, the maximum immiscibility is predicted at a symmetric solvent composition. Interplay of the two driving forces gives rise to a reentrant behavior in which cononsolvency of the two types switching from one to the other, through a "conventional" region where overall solvent quality varies monotonically with the solvent composition. The RPA model developed in this work provides a unified analytical framework for understanding the conformational and solubility transition of polymers in multi-solvent mixtures. Findings of such highlight the complex role played by the solvents in polymer solutions, a problem of fundamental and practical interest in diverse applications of materials science.

I. Introduction

Polymer solutions of mixed solvents are often encountered in experiments, as a means of tuning miscibility, manipulating polymer assemblies, or simply as the byproducts of processing history. Effects of having mixed solvents in polymer solutions are however far from being trivial. An exemplary situation is the so-called cononsolvency, in which polymers dissolved in a mixture of good solvents show a puzzling reentrant collapse and swelling transition.[1-4] Theoretical understanding of cononsolvency has first arrived from chemistry-specific computer simulations of thermo-sensitive polymers in solvent mixtures.[3,5-8] Later on, Tanaka et al.[9] show that cononsolvency of temperature-sensitive polymers can be explained based on the competition between the two solvents in forming hydrogen bonds with polymers. They found that the total coverage of the polymer chain by bound solvent molecules is not a monotonic function but passes through a minimum at the composition where the competition is strongest. However, it has long been known that polymers with upper critical solution temperature (UCST), and even standard polymers, such as polystyrene[10-12] also display the cononsolvency behavior, pointing to the possible generic origin of this enigmatic phenomenon.

Computer simulations based on the generic bead-spring model were performed by Mukherji et al. [13] to understand the coil-globule-coil transition of polymers in mixtures of two good solvents. They attribute the initial collapse to the formation of bridges that the cosolvent molecules form by binding two monomers far apart along the polymer backbone, and the reopening at higher cosolvent concentrations is due to the increased decoration of the polymer by cosolvent molecules. Their study show that chemistry-specific details are indeed unnecessary for a system to display cononsolvency in computer simulations, on the other hand the discrete nature of the proposed mechanism — preferential solute–(co)solvent coordination, implies that Flory-Huggins type mean-field theories may not be sufficient to describe such behavior. Simulations using similar bead-spring model have also been reported in a number of other contexts.[14-17] In addition to the bead-spring model, Zhang et al. shows that computer simulations employing the mesoscopic hybrid model can also reproduce the cononsolvency behavior.[18] The non-bonded interactions in the hybrid model are templated by functionals of local order parameters that are similar to free energies in classical density functional theory. Conceptually different from conventional microscopic descriptions, the success of the mesoscopic hybrid model in capturing the cononsolvency effect further indicates the universality of this phenomenon.

General analytical theories have played an especially important role in interpreting the cononsolvency from a generic perspective. Using the standard Flory-Huggins theory, Dudowicz et al.[19] find that polymer miscibility patterns in solvent mixtures are largely controlled by the solvent-(co)solvent interaction energies. In particular, when solvent-(co)solvent interaction parameter is negative and exceeds in magnitude the polymer-solvent interactions (for instance, when the solvent and cosolvent molecules contain polar groups or form a weak hydrogen bonding), cononsolvency arises with the maximum immiscibility being predicted at equal solvent-cosolvent fraction. On the other hand, a Langmuir-like thermodynamic treatment is devised by Mukherji et al.[20] to account for solvent-mediated bridging and competitive displacement of different solvent components onto the polymer. In the model, cosolvents adsorptions are categorized into two different modes: bridge-forming and non-bridge-forming, and a free energy density is prescribed to account for the difference. Collapse and swelling transition results from changes in the relative fraction of the two adsorption modes that minimizes the free energy density. In the same vein, Sommers[21,22] proposed the adsorption−attraction model which simplifies the free energy model in Ref [20] by introducing a free energy term to account for the mean-field attraction between monomers due to the "bridging effect" mediated by adsorbed cosolvents. In contrast to Ref [19], the driving force of polymer cononsolvency in Ref. [20] and [21] is the difference in the affinity between polymer and the two solvents, with solvents and cosolvents forming ideal mixtures with each other with zero enthalpy/entropy of mixing. Furthermore, Ref. [20] and [21] predict that polymers possess the most collapsed conformations when the cosolvents (the better solvent for the polymers) being the minor solvent as opposed to the equal fraction predicted in Ref [19].

In this study, we aim to explore the common generic cause underlying the two types of cononsolvency behaviors reported in the literature.[13,18-21] By calculating the partial structure factors of ternary polymer solutions using the random phase approximation (RPA) approach, we show that both types of polymer cononsolvency can be rationalized through the lens of mean-field density correlations, without the need of introducing *ad hoc* topological correlations (such as the solvent-mediated bridging) and the corresponding energetic parameters. The manuscript is organized as the following: The RPA model of ternary polymer solutions is briefly discussed in Section II. Two special cases are then employed for illustrating two different mechanisms that lead to polymer cononsolvency in ternary solutions. In Section III, calculations are carried out to quantitatively describe the dependence of overall solvent quality and the phase behavior of polymer solutions on solvent composition under the two types of cononsolvency effects. In Section IV, discussions are extended to general situations where cononsolvency behavior is controlled by the interplay/interference of the two identified mechanisms.

II. The Random Phase Approximation Model of Ternary Polymer Solutions

The ternary RPA model is applied here to the mixture of a homopolymer P and two solvents — solvent S and cosolvent C.[23-25] In particular, the polymer-polymer partial structure factor is given by:

$$\frac{1}{S_{PP}(q)}=\frac{1}{S_{PP}^{0}(q)}+\frac{1-2\chi_{PS}\phi_S-2\chi_{PC}\phi_C}{[\mathrm{c}-2\chi_{SC}\phi_S\phi_C]}-\frac{\phi_S\phi_C[(\chi_{PS}-\chi_{PC})^2+\chi_{SC}^2-2\chi_{SC}(\chi_{PS}+\chi_{PC})]}{[\mathrm{c}-2\chi_{SC}\phi_S\phi_C]}\#(1)$$

in which $S_{PP}^{0}(q)$ is the non-interacting single chain structure factor, the total solvent volume fraction $c\equiv\phi_S+\phi_C=1-\phi_P$ with ϕ_i being the volume fraction of component i, and χ_{ij} is the Flory-Huggins immiscibility parameter between component i and j. In Equation (1), for simplicity, the specific volumes of all components have been assumed to be identical and of unity. A systematic study on the effects of asymmetric specific volumes on the polymer cononsolvency behavior will be reported in future work. For a single-solvent system ($\phi_C=0$), the above equation reduces to the known result:

$$\frac{1}{S_{PP}(q)}=\frac{1}{S_{PP}^{0}(q)}+\frac{1}{\phi_S}-2\chi_{PS}\#(2)$$

. The last two terms $\frac{1}{\phi_S}-2\chi_{PS}$ determines the solvent quality for polymers in a single-solvent polymer solution. $\frac{1}{\phi_S}-2\chi_{PS}>0$ and <0 distinguish the good and bad solvent conditions, respectively, and $\frac{1}{\phi_S}-2\chi_{PS}=0$ defines the θ-solvent condition at which the excluded volume and immiscibility effects offset each other.

As to binary-solvent polymer solutions, we restrict our attention to solutions with the two solvents being perfectly miscible, i.e., $\chi_{SC}\leq 0$, and without losing generality, we designate the cosolvent C as the better solvent for polymers, i.e, $\chi_{PC}\leq\chi_{PS}$. In analogy to Eq. (2), the overall solvent quality can be defined as:

$$\Gamma=\frac{1-2\chi_{PS}\phi_S-2\chi_{PC}\phi_C}{[\mathrm{c}-2\chi_{SC}\phi_S\phi_C]}-\frac{\phi_S\phi_C[(\chi_{PS}-\chi_{PC})^2+\chi_{SC}^2-2\chi_{SC}(\chi_{PS}+\chi_{PC})]}{[\mathrm{c}-2\chi_{SC}\phi_S\phi_C]}$$

$$= \frac{1 - \chi_{SC}{}^{2}\phi_S\phi_C}{c'} - 2\left[\frac{(1 - x'_C + x'_S)}{2}\chi_{PS} + \frac{(1 - x'_S + x'_C)}{2}\chi_{PC} + \frac{c'}{2}x'_S x'_C \Delta\chi^2\right] \#(3)$$

, in which $\Delta\chi \equiv (\chi_{PS} - \chi_{PC}) > 0$ and $c' \equiv c - 2\chi_{SC}\phi_S\phi_C$, $x'_C \equiv \frac{\phi_S}{c'}$ and $x'_S \equiv \frac{\phi_C}{c'}$ are the *effective* solvent volume fraction and solvent compositional fraction, respectively. The first term in Eq. (3) accounts for the *effective* excluded volume effect that takes into consideration of the less extent of mixing between polymers and solvent molecules due to the preferential mixing by the two solvents. The three terms inside the square bracket represent the overall immiscibility between the polymer and the solvent mixture. The first two terms correspond to a mixing-rule by a weighted average. The term $\frac{c'}{2}x'_S x'_C \Delta\chi^2 > 0$ (if χ_{PS} and χ_{PC} being different) always contributes to *reducing* the overall solvent quality. The effects of varying solvent composition (i.e., varying ϕ_S and ϕ_C at constant ϕ_P) on Γ can be better illustrated by considering two special cases: (1) the ideal-mixing binary solvent mixture, i.e., $\chi_{SC} = 0$; and (2) the equal-quality binary solvent mixture, i.e., $\Delta\chi = 0$. In the next, we will discuss the two cases separately to elucidate the respective mechanisms that are responsible for the polymer cononsolvency behavior.

II.1 The ideal-mixing binary solvent mixture ($\chi_{SC} = 0$)

With $\chi_{SC} = 0$, there is $c' = c$, and $x'_S = \frac{\phi_S}{c} \equiv x_S$ and $x'_C = \frac{\phi_C}{c} \equiv x_C$ recover the physical meaning of true solvent compositional fractions of S and C, respectively. Eq. (3) becomes

$$\Gamma = \frac{1}{c} - 2\left[(x_S\chi_{PS} + x_C\chi_{PC}) + \frac{c}{2}x_S x_C \Delta\chi^2\right] \#(4)$$

. In this case, the excluded volume effect, $\frac{1}{c} = \frac{1}{1 - \phi_P}$, is the same as that in the single-solvent system due to ideal-mixing of the two solvents. The mixing rule contributes a linear change to Γ as x_C being varied, while the term $\frac{c}{2}x_S x_C \Delta\chi^2$ possesses a maximum at $x_S = x_C = 0.5$ that gives rise to a minimum in Γ. The location of the minimum can be determined by solving $\left.\frac{d\Gamma}{dx_C}\right|_{x_C = x_C^*} = 0$ that gives

$$x_C^* = \frac{1}{2} - \frac{1}{c\Delta\chi} \#(5)$$

. The condition for the minimum $\Gamma_{\min}$ to occur between $0 < x_C^* < 1$ is then given by

$$\Delta\chi > \frac{2}{c} \equiv \Delta\chi^{\text{conon}} \ \#(6)$$

. The presence of a minimum in Γ implies that the overall solvent quality for polymers deteriorates upon the addition of cosolvents of a better quality, which serves as the definition of cononsolvency in this study. Equation (6) suggests that cononsolvency is a generic effect that is expected to occur for many polymers as long as one of the solvents is significantly better than the other. Moreover, Γ_{min} is predicted to occur at *non*-equal-fraction i.e., $0 < x_C^* < 0.5$, a net outcome under the combined effect of the mixing-rule and the term $\frac{\text{c}}{2} x_S x_C \Delta\chi^2$. The critical value of $\Delta\chi$ for the ternary polymer solution falling into the bad-solution condition can be determined from the euqation Γ_{min} $(\Delta\chi = \Delta\chi^{\theta}) = 0$, i.e.:

$$-c x_S^* \, x_C^* \, \Delta\chi^2 + 1/\text{c} - 2\left(x_S^* \, \chi_{PS} + x_C^* \, \chi_{PC}\right) = 0 \ \#(7)$$

, of which $\Delta\chi^{\theta}$ is the positive root. The critical value of $\Delta\chi$ for the ternary polymer solution to undergo phase transition can be determined from the spinodal instability criterion by requiring $\frac{1}{S_{PP}(0)} = \frac{1}{S_{PP}^{0}(0)} + \Gamma_{\text{min}}(\Delta\chi = \Delta\chi^{\text{demix}}) = 0$ that gives:

$$\Delta\chi^{\text{demix}} = \left[\frac{1}{c x_C^* \, x_S^* \, S_{PP}^{0}(0)} + \frac{1}{c^2 x_C^* \, x_S^*} - \frac{2}{c}\left(\frac{\chi_{PS}}{x_C^*} + \frac{\chi_{PC}}{x_S^*}\right)\right]^{\frac{1}{2}} \#(8)$$

II.2 The equal-quality binary solvent mixture ($\Delta\chi = 0$)

On the other hand, with $\Delta\chi = 0$, Eq. (3) becomes

$$\Gamma = \frac{1 - {\chi_{SC}}^2 \phi_S \phi_C}{c - 2\chi_{SC} \phi_S \phi_C} - 2\chi_{PS} \ \#(9)$$

. In this case, the effect of polymer-solvent immiscibility is identical to that in a single-solvent system, as expected since the two solvents behave identically from the perspective of polymers. At a given polymer volume fraction ϕ_P, the effective excluded volume effect exhibits a minimum at $x_S = x_C = 0.5$, giving rise to a minimum in Γ at the same solvent composition. Note that the presence of a minimum in Γ occurs as long as $\chi_{SC} < 0$ and is independent of χ_{PS} or χ_{PC}. On the other hand, the exact value of the minimum, Γ_{min}, depends on c, χ_{SC}, and χ_{PS}. Similar to the "ideal-mixing" case, the critical value of χ_{SC} for the ternary solution being in the bad-solution condition can be solved from the equation $\Gamma_{\text{min}}(\chi_{SC} = \chi_{SC}^{\theta}) = 0$:

$$\frac{1-\frac{{\chi_{SC}^{\theta}}^{2}}{4}}{c-\frac{\chi_{SC}^{\theta}}{2}}-2\chi_{PS}=0 \ \#(10)$$

, and the critical value of χ_{SC} for the ternary solution to undergo phase transition can be solved from the equation $\frac{1}{S_{PP}^{0}(0)}+\Gamma_{\min}\left(\chi_{SC}=\chi_{SC}^{\text{demix}}\right)=0$:

$$\frac{1}{S_{PP}(0)}=\frac{1}{S_{PP}^{0}(0)}+\frac{1-\frac{{\chi_{SC}^{\text{demix}}}^{2}}{4}}{c-\frac{\chi_{SC}^{\text{demix}}}{2}}-2\chi_{PS}=0 \ \#(11)$$

III. RPA Calculations

In this section, calculations based on the RPA model are carried out to quantitatively describe the effect of varying solvent composition on the overall solvent quality and the phase behavior of ternary polymer solutions. For simplicity, we set $\chi_{PS}=0$, and adopt the continuum Gaussian chain model for the non-interacting single chain structure factor, i.e., $S_{PP}^{0}(q)=N\phi_{P}g_{D}(x)$, where N is the degree of polymerization, ϕ_{P} is the polymer volume fraction, and $g_{D}(x\equiv\frac{N}{6}(bq)^{2})$ is the Debye function with b and q being the statistical segment length and magnitude of the wave vector, respectively.

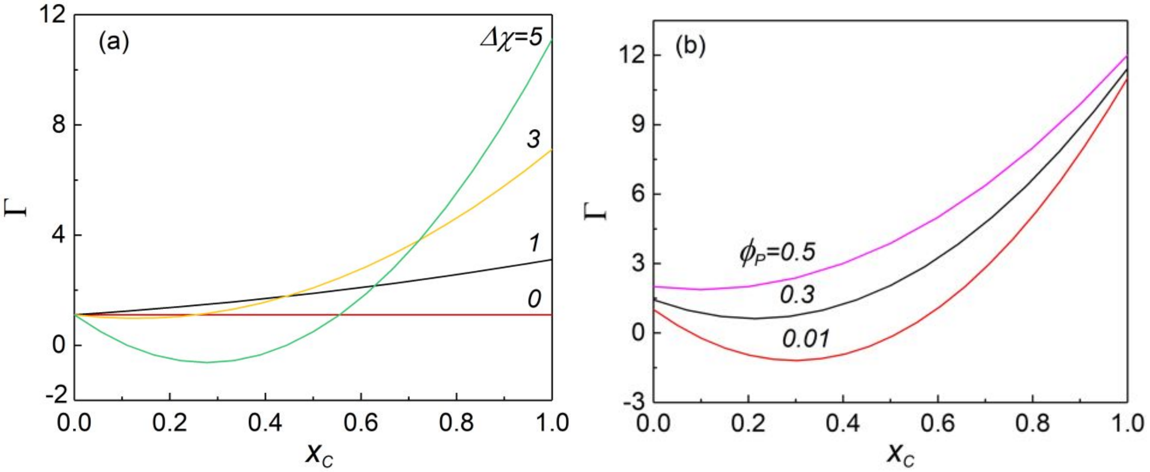

Figure 1: The overall solvent quality Γ as the function of cosolvent composition x_c calculated with $N=50$ at (a) varying $\Delta\chi$ and $\phi_P=0.1$; and (b) varying ϕ_P and $\Delta\chi=5$.

III.1 The ideal-mixing binary solvent mixture ($\chi_{SC} = 0$).

Figure 1(a) shows the overall solvent quality Γ as the function of the cosolvent fraction x_C at $\phi_P = 0.1$. With $\Delta\chi < \frac{2}{1-\phi_P} \sim 2.2$, the overall solvent quality monotonically improves with increasing x_C. Beyond this value, a minimum in Γ starts to develop with larger $\Delta\chi$ values producing greater reductions in Γ. As x_C further increases, the overall solvent quality starts to recover, and the rate of recovering is faster with greater $\Delta\chi$. For $\Delta\chi \gtrsim 4.4$, Γ becomes negative at certain range of x_C indicating that the solution falls into the bad-solvent condition. For a given $\Delta\chi$ ($\Delta\chi = 5$), Figure 1(b) shows that the cononsolvency effect becomes abated with increasing polymer concentration. Both the range of x_C in which Γ decreases and degree of reduction shrinks at higher ϕ_P. With $\phi_P > 1 - \frac{2}{\Delta\chi} = 0.6$ the curves become strictly monotonic, with Γ increasing gradually with increasing x_C. It is worth mentioning that the predicted dependence of Γ on x_C does not depend on the form of S^0_{PP} to be assumed by the RPA model.

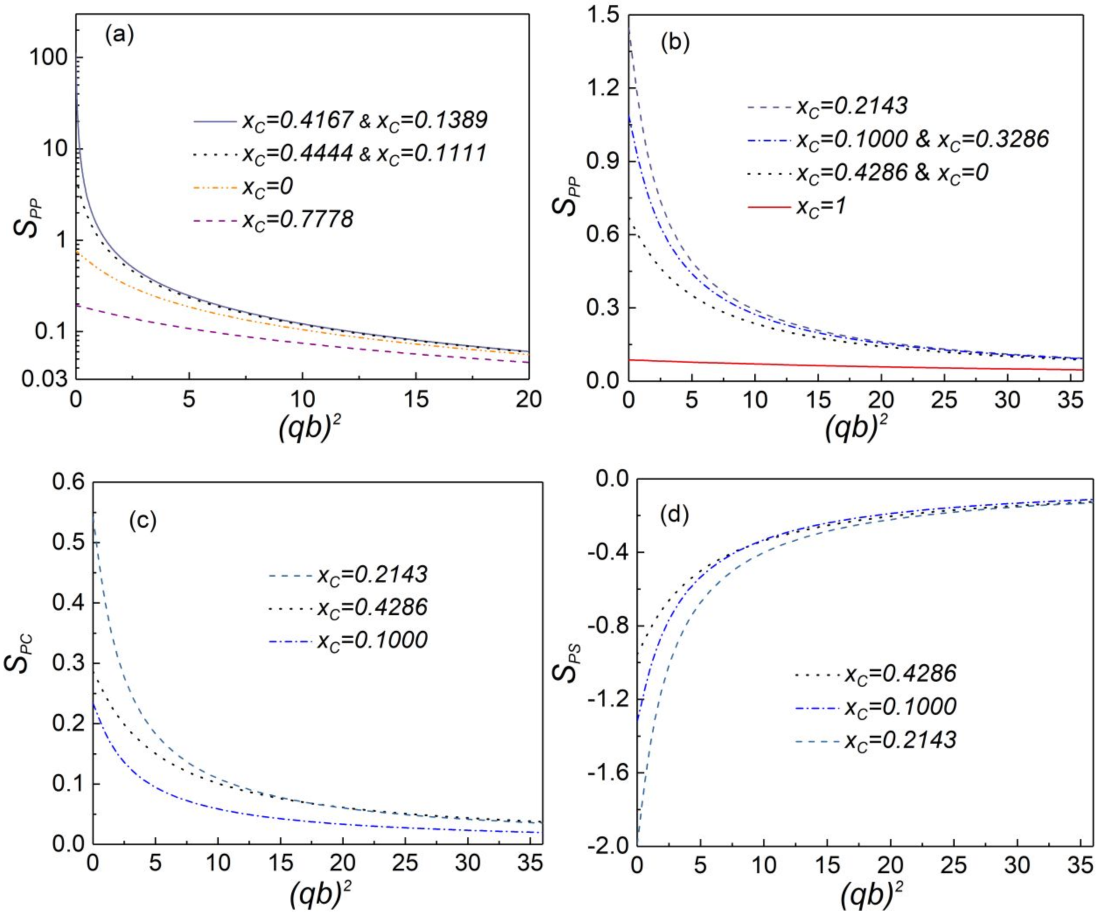

Figure 2: Evolution of the partial structure factors with changing cosolvent composition x_C calculated with $N = 50$ at: (a) $\phi_P = 0.1$, (b)-(d) $\phi_P = 0.3$.

At $\Delta\chi = 5$, Figure 2 (a) and (b) show evolution of the partial structure factor $S_{PP}(q)$ with solvent composition x_C at $\phi_P = 0.1$ and $\phi_P = 0.3$, respectively. At $\phi_P = 0.1$, Figure 2(a) shows a diverging trend for $S_{PP}(q = 0)$ as x_C approaches 0.4152 (from above) and 0.1403 (from below), signaling phase instability in this range of solvent composition. At higher polymer concentration $\phi_P = 0.3$, $S_{PP}(q = 0)$ stays finite for all solvent composition with $S_{PP}(q)$ obtained at $x_C = 0.2143$ lying above all other curves. In the meanwhile, the corresponding behavior of S_{PC} and S_{PS} shown in Figure 3 (c)-(d) indicates the relative enrichment of cosolvents and depletion of solvents around polymers. At even higher polymer concentration $\phi_P = 0.7$, cononsolvency effect is no longer observable and $S_{PP}(q)$ flattens gradually with increasing x_C (data not shown).

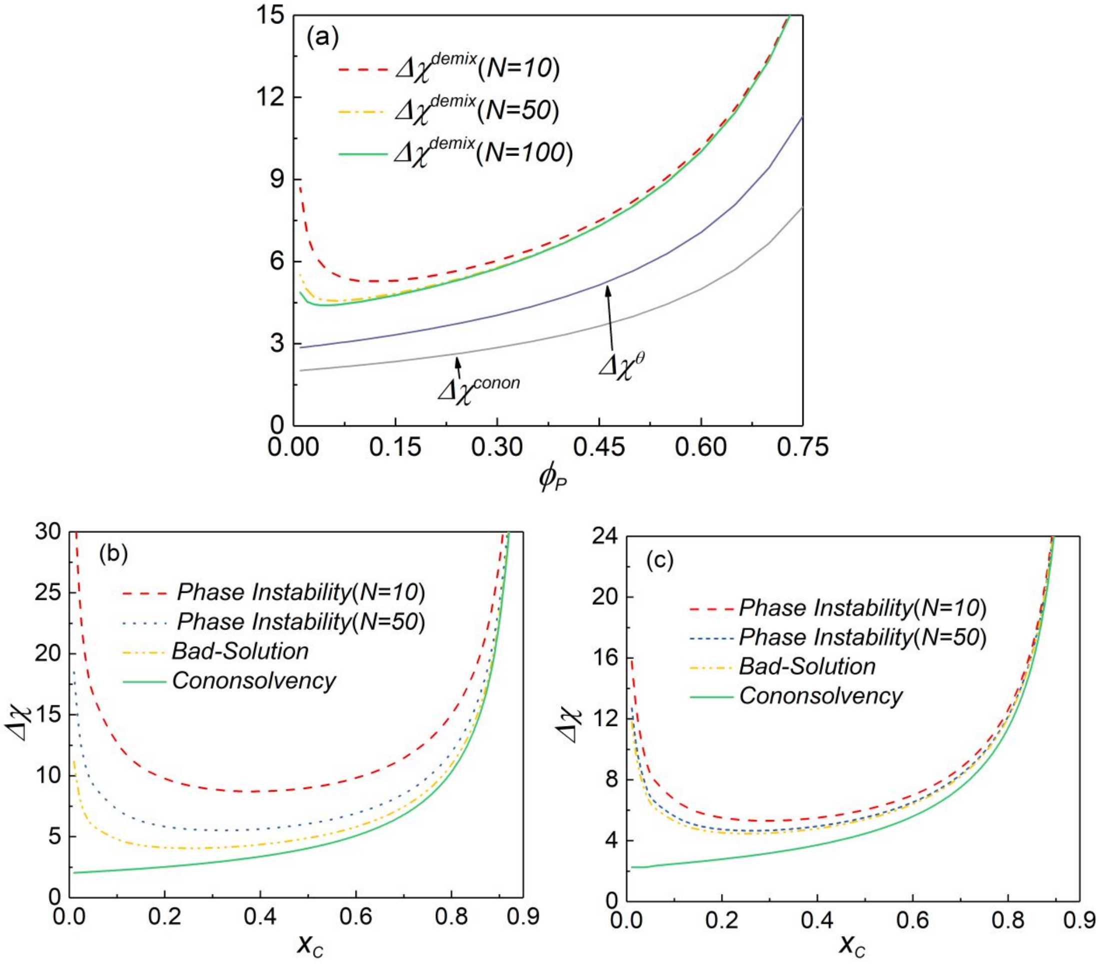

Figure 3: (a) The critical values $\Delta\chi^{\mathrm{con}}$, $\Delta\chi^{\theta}$, and $\Delta\chi^{\mathrm{demix}}$ as the function of ϕ_P. (b)-(c) Boundaries of cononsolvency, bad-solution condition, and phase instability in the $\Delta\chi$-x_c plane for $\phi_P = 0.01$ and 0.1.

Figure 3(a) shows the dependence of the critical values $\Delta\chi^{\mathrm{conon}}$, $\Delta\chi^{\theta}$and $\Delta\chi^{\mathrm{demix}}$ on polymer concentration. While $\Delta\chi^{\mathrm{conon}}$ and $\Delta\chi^{\theta}$monotonically increases with ϕ_P, $\Delta\chi^{\mathrm{demix}}$ shows an increase approaching to the dilute limit due to the enhanced translational entropy. The effect of chain length on $\Delta\chi^{\mathrm{demix}}$ is only appreciable at low polymer concentrations. Furthermore, at given ϕ_P and $\Delta\chi$, the respective range of x_C within which cononsolvency, the bad-solution condition, and phase instability occur can be determined from Eq. (6)-(8). Figure 3 (b)-(c) show such phase diagrams for two polymer concentrations $\phi_P = 0.01$ and 0.1, respectively. When $\Delta\chi^{\mathrm{conon}} < \Delta\chi < \Delta\chi^{\theta}$ the ternary solution exhibits a deterioration in the overall solvent quality as x_C increases and then recover, but remains in the good-solution condition (i.e., $\Gamma > 0$) for all x_C. As $\Delta\chi^{\theta} < \Delta\chi$, the solution will fall into the bad-solution condition with increasing x_C. Figure 3(b) suggests that the polymers may undergo a reentrant coil-globule-coil transition without experiencing a phase instability, consistent with findings in Ref. [20] that polymer conformational changes under the cononsolvency effect may not correspond to a phase transition. However, such behavior may no longer be possible at higher polymer concentrations or higher molecular weight, as the boundaries for the bad-solution condition and phase instability almost overlap with each other (Figure 3(c)).

III.2 The equal-quality binary solvent mixture ($\Delta\chi = 0$).

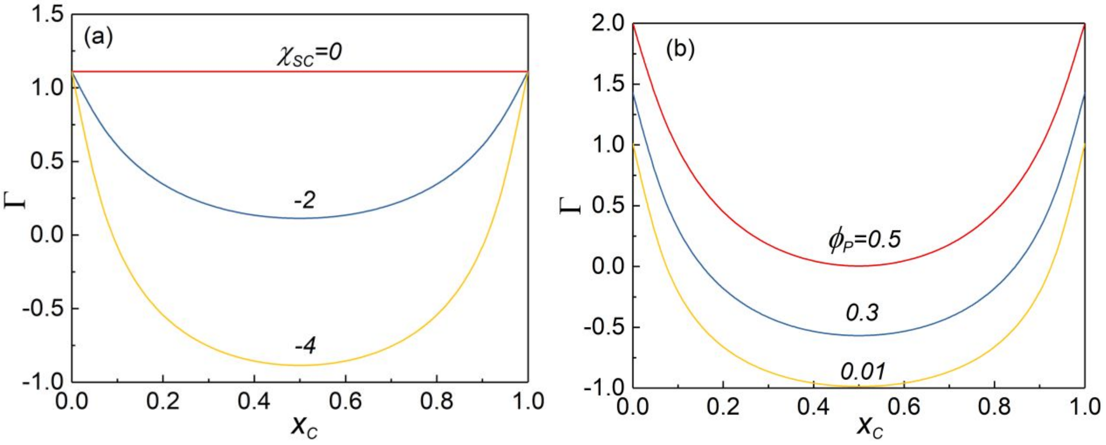

Figure 4: The overall solvent quality Γ as the function of solvent composition x_c calculated with $N = 50$ at (a) varying χ_{SC} and $\phi_P = 0.1$; and (b) varying ϕ_P and $\chi_{SC} = -4$.

Figure 4 (a) and (b) shows the overall solvent quality as function of x_C at $\phi_P = 0.1$ and $\chi_{SC} = -4$, respectively. The minimum in Γ is always observed at $x_C = 0.5$ as long as $\chi_{SC} < 0$, with smaller χ_{SC} and ϕ_P values producing greater drops in Γ. The dependences of the critical values ${\chi_{SC}}^{\mathrm{conon}}$, ${\chi_{SC}}^{\theta}$and ${\chi_{SC}}^{\mathrm{demix}}$ on polymer concentration are shown Figure 5(a), and Figure 5(b)-(c) show the phase diagrams of the ternary solution at two polymer concentrations $\phi_P = 0.01$ and 0.1, respectively. Similar to the ideal-mixing case, at low polymer concentration polymers may undergo a reentrant coil-globule-coil transition without demixing. In contrast to the idea-mixing system, the overall solvent quality and the phase diagrams of equal-quality mixing systems are symmetric about $x_C = 0.5$, as suggested by Equation (9), which agrees with the findings in Ref. [19] that the ternary solution behaves identically with $\frac{x_C}{x_S} = r$ or $\frac{x_S}{x_C} = r$.

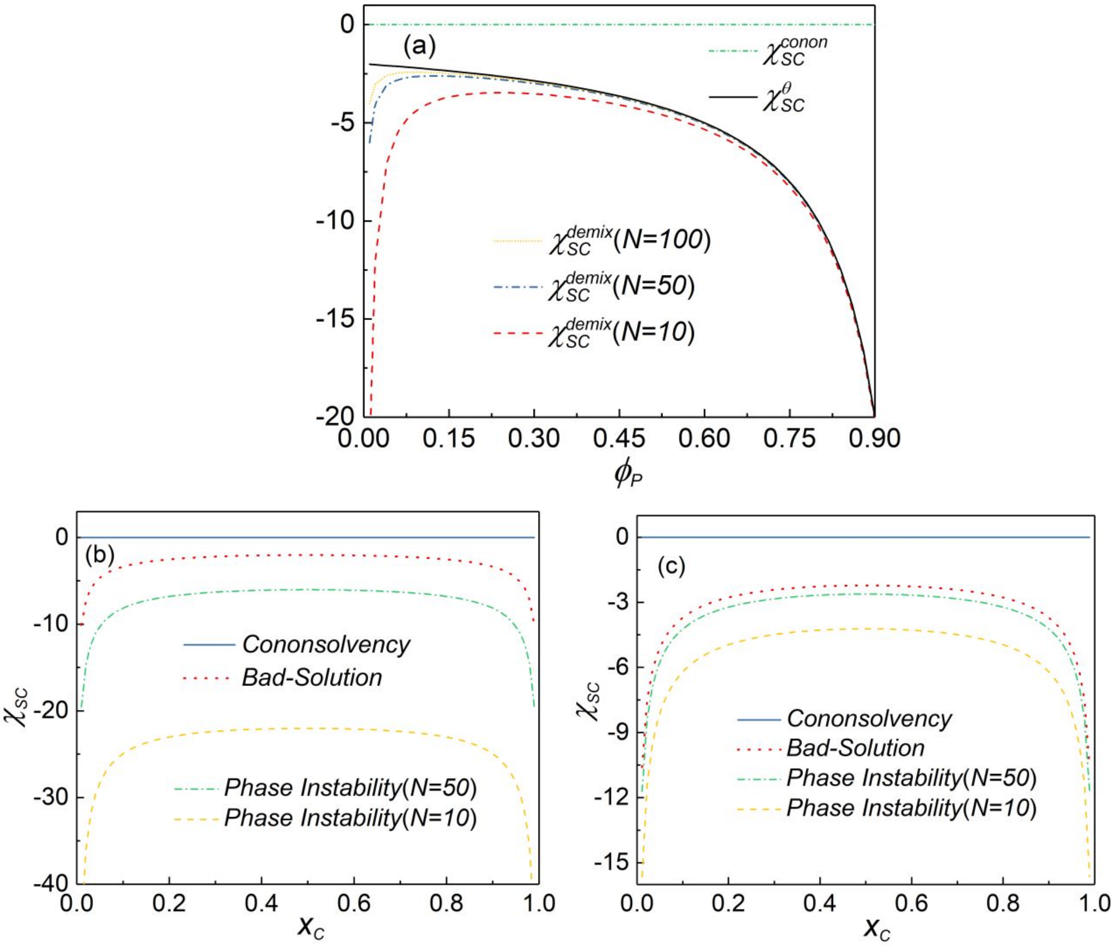

Figure 5: (a) $\chi_{SC}{}^{\mathrm{conon}}$, $\chi_{SC}{}^{\theta}$and $\chi_{SC}{}^{\mathrm{demix}}$ as the function of ϕ_P calculated from Eq. (6), (10), (11) with $N = 10, 50,$ and 100. (b)-(c) Boundaries of cononsolvency, bad-solution condition, and phase instability in the χ_{SC}-x_c plane for $\phi_P = 0.01$ and 0.1.

IV. Discussion

Results in Section II and III describe the two situations where cononsolvency of polymers in ternary solutions are driven by preferential solvation of polymers (when $\chi_{SC} = 0$ and $\Delta\chi > 0$) and the preferential mixing of solvents (when $\chi_{SC} < 0$ and $\Delta\chi = 0$), respectively. In general situations where $\Delta\chi \geq 0$ and $\chi_{SC} \leq 0$, it is expected that both effects play a part in affecting the conformational and phase-behavior changes with varying solvent composition. Generally, with $\Delta\chi$ ≥ 0 and $\chi_{SC} \leq 0$, $\frac{\partial\Gamma}{\partial\phi_C} = 0$ becomes a quadratic equation in terms of $(2x_C - 1)$:

$$-\chi_{SC}\Delta\chi(2x_C-1)^2+\left(\Delta\chi^2+\chi_{sc}^2-\frac{2\chi_{SC}}{c}\right)(2x_c-1)+\Delta\chi\left(\frac{2}{c}-\chi_{SC}\right)=0\ \#(12)$$

that gives two roots

$$r_{1,2}=\frac{-\left(\Delta\chi^2+\chi_{SC}^2-\frac{2\chi_{SC}}{c}\right)\pm\sqrt{\left(\Delta\chi^2-\chi_{SC}^2+\frac{2\chi_{SC}}{c}\right)^2}}{-2\chi_{SC}\Delta\chi}\#(13)$$

. The physical constraint $-1 \leq r_1 < r_2 \leq 1$ determines the conditions under which extremity in Γ can be observed. It can be proved that the two roots have the same sign. Also,

$$r_1+r_2=\frac{\left(\Delta\chi^2+\chi_{SC}^2-\frac{2\chi_{SC}}{c}\right)}{\chi_{SC}\Delta\chi}>\frac{\left(-2\chi_{SC}\Delta\chi-\frac{2\chi_{SC}}{c}\right)}{\chi_{SC}\Delta\chi}=-2-\frac{2}{c\Delta\chi}<-2\#(14)$$

which implies that it is only possible for the larger root r_2 (at which Γ is at minimum) to satisfy the constraint $-1 < r_2 < 1$. For this to be the case, the following conditions need to be satisfied:

$$(\Delta\chi+\chi_{SC})\geq\tfrac{2}{c},\ \text{when } \Delta\chi^2-\chi_{SC}^2+2\chi_{SC}/c>0$$

$$(\Delta\chi+\chi_{SC})\leq 0,\ \text{when } \Delta\chi^2-\chi_{SC}^2+2\chi_{SC}/c<0.$$

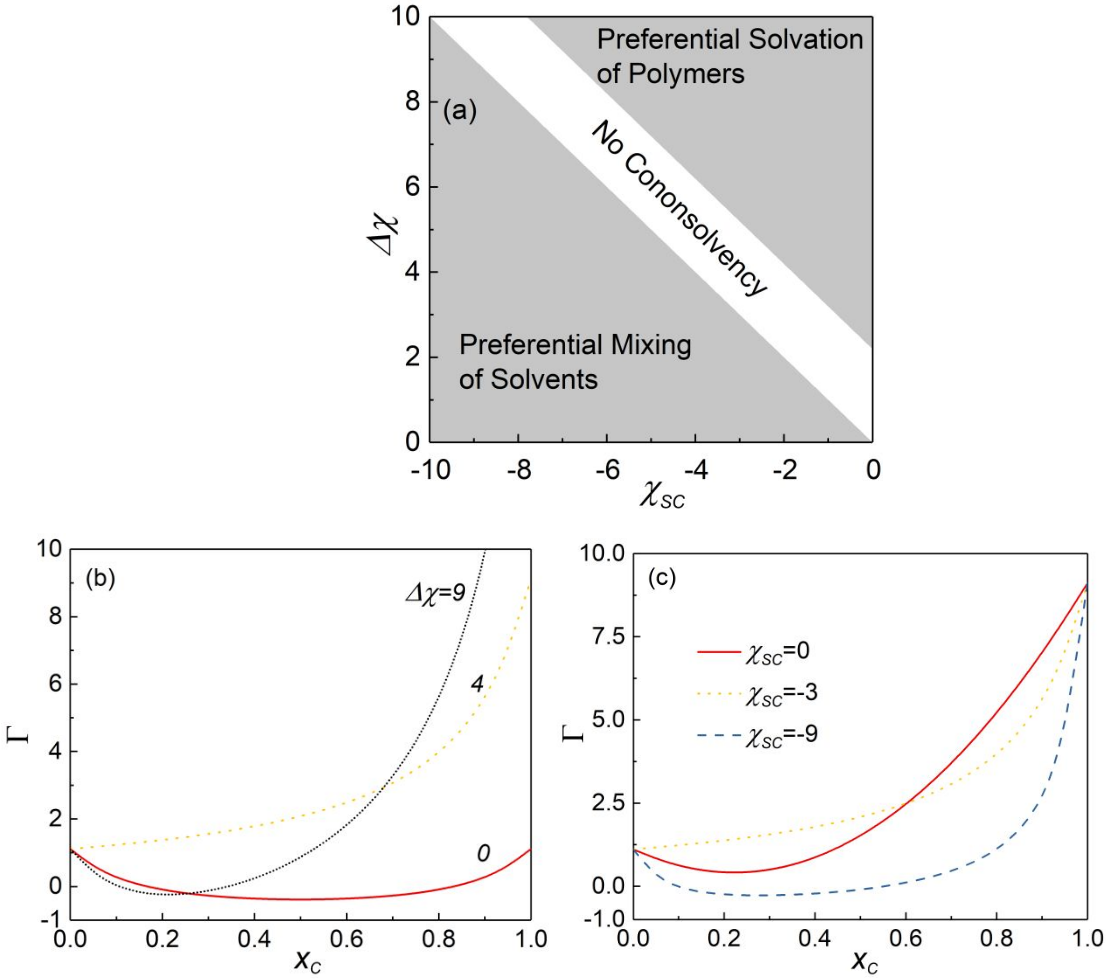

Figure 6: (a) The parameter region in the $\Delta\chi$-χ_{SC} plane where cononsolvency will (the shaded area) and will not (the blank area) occur with $\phi_P = 0.1$. The overall solvent quality Γ as the function of solvent composition x_c calculated (by setting $\chi_{PS} = 0$) at (b) varying $\Delta\chi$ with $\phi_P = 0.1$ and $\chi_{SC} = -3$; and (c) varying χ_{SC} with $\phi_P = 0.1$ and $\Delta\chi = 4$.

This set of conditions give rise to two separate regions in which cononsolvency will occur in the $\Delta\chi$-χ_{SC} plane (shaded area in Figure 6(a)). In the lower region ($\Delta\chi \leq -\chi_{SC}$), cononsolvency is driven by the preferential mixing of the two solvents and therefore independent of polymer volume fraction. In the upper region ($\Delta\chi \geq \frac{2}{c} - \chi_{SC}$), cononsolvency is driven by the preferential solvation of polymers. In-between, cononsolvency is suppressed by the counter-acting of the two effects (i.e., the effect of $c' \neq c$ is felt by both the excluded volume and immiscibility terms in Equation (3)). By setting $\chi_{PS} = 0$ (for simplicity), Figure 6 (b) and (c) depict such "reentrant" behavior of cononsolvency, with $\Gamma(x_c)$ exhibiting nonmonotonic variations by either increasing or decreasing $\Delta\chi$ and χ_{SC}, respectively, — suggesting the two effects switching their roles as the driving force behind the cononsolvency behavior.

Another aspect of generalizing the current RPA analysis concerns the specific volumes. Although in the current RPA calculations, the specific volume of each component is assumed to be identical, an extension to the treatment of asymmetric specific volumes under the RPA framework should be straight forward. The effects of asymmetric specific volumes between the solvent and cosolvent on the RPA predictions can, nevertheless, be estimated based on the consideration of mixing entropy. In general, asymmetry in the specific volumes will lead to less degree of mixing between the solvents and cosolvents. For the cononsolvency driven by the "preferential solvation of polymers", this will promote the mixing between polymer sand cosolvents. As the result, the predicted values of $\Delta\chi^{\mathrm{conon}}$, $\Delta\chi^{\theta}$ and $\Delta\chi^{\mathrm{demix}}$ will be smaller and Γ_{min} will move to smaller x_c values. As to the cononsolvency driven by the "preferential mixing of solvents", asymmetry in the specific volumes will move the maximum mixing away from $x_c = 0.5$ and renders the phase diagrams shown in Figure 5 asymmetric about $x_c = 0.5$.

In accounting for the cononsolvency effect due to preferential solvation of polymers, previous theoretical studies[20,21] often rely on introducing the concept of "mediated bridging" between monomers. In the meanwhile, the fundamental role played by the mean-field density correlations on the cononsolvency effect has been largely overlooked. To the best knowledge of the authors, the RPA model of ternary polymer solutions applied in this study represents the first attempt of highlighting this point. Under the RPA framework, the two types of cononsolvency effects can be unified under the same concept of mean-field density correlations (polymer-cosolvents and solvents-cosolvents correlations, respectively). On the other hand, the current RPA model predicts unusually large values of $\Delta\chi$ for the polymer cononsolvency to occur. From a mean-field point of view, large values of the Flory-Huggins parameter often indicate the presence of strong associative interactions (such as polymer solutions with hydrogen bonding). It is also possible that $\Delta\chi$ has been overestimated in the current RPA calculations. One reason may come from assuming the continuum Gaussian chain model for the single-chain structure factor, $S_{\mathrm{PP}}^{0}(q)$. A more rigorous treatment would be to calculate it in a self-consistent manner. Another plausible cause for the overestimate of $\Delta\chi$ is the mean-field nature of the RPA approach, in which the possibly strong topological correlations between the polymer segments (such as the "mediated bridging" effect) are not accounted for.[22] Further study will be required to allow the clarification of the source of overestimate.

In summary, the RPA model offers a clear picture about the generic origin(s) of polymer cononsolvency in solvent mixtures. The study reveals the complex roles played by solvents in determining conformation and solubility transitions of polymers in multi-solvent mixtures. Theoretical understandings as such offer a rationale guideline for the potential use of solvent composition as an extra degree of freedom for controlling and modulating polymer self-assemblies in solutions (e.g. polymer brushes and micellar solutions, etc.). Studies along this line is underway.

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