A statistical theory of coil-to-globule-to-coil transition of a polymer chain in a mixture of good solvents

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Abstract – We present an off-lattice statistical model of a single polymer chain in mixed-solvent media. Taking into account the polymer conformational entropy, renormalization of solvent composition near the polymer backbone, the universal intermolecular excluded-volume and van der Waals interactions within the self-consistent field theory, the reentrant coil-to-globule-to-coil transition (co-nonsolvency) has been described in this paper. For convenience we split the system volume in two parts: the volume occupied by the polymer chain and the volume of bulk solution. Considering the equilibrium between two sub-volumes, the polymer solvation free energy as a function of radius of gyration and co-solvent mole fraction within internal polymer volume has been obtained. Minimizing the free energy of solvation with respect to its arguments, we show two qualitatively different regimes of co-nonsolvency. Namely, at sufficiently high temperature the reentrant coil-to-globule-to-coil transition proceeds smoothly. On the contrary, when the temperature drops below a certain threshold value a coil-globule transition occurs in the regime of first-order phase transition, i.e., discontinuous changes of the radius of gyration and the local co-solvent mole fraction near the polymer backbone. We show that, when the collapse of the polymer chain takes place, the entropy and enthalpy contributions to the solvation free energy of the globule strongly grow. From the first principles of statistical thermodynamics we confirm earlier speculations based on the MD simulations results that the co-nonsolvency is the essentially enthalpic-entropic effect and is caused by enthalpy-entropy compensation. We show that the temperature dependences of the solution heat capacity change due to the solvation of the polymer chain are in qualitative agreement with the differential scanning calorimetry data for PNIPAM in aqueous methanol.

Introduction. – Co-nonsolvency (insolubility of a polymer in a mixture of two good solvents) is one of the most intriguing phenomena in physical chemistry of polymers. Despite the great efforts in both experimental [1–9] and theoretical [10–18] investigations in understanding the co-nonsolvency, the mechanism of this phenomenon remains unclear until now [18].

Basing on the results of the experimental researches devoted to the behavior of the single poly(N-isopropylacrylamide) (PNIPAM) polymer chain [1–3] as well as the behavior of PNIPAM hydrogels [1,5], Tanaka et al. [10] formulated a quasi-chemical model of a single PNIPAM chain in a mixed water-methanol solvent. The authors showed that the co-nonsolvency occurs due to a competition of water and methanol molecules for hydrogen bonding with the polymer backbone. Thus, it seemed that the co-nonsolvency is caused by the hydrogen bonding between solvent molecules and monomers. However, in recent papers of Mukherji et al. [11–13] by using MD computer simulations of a Lennard-Jones polymer chain dissolved in a two-component Lennard-Jones mixed solvent it was shown that co-nonsolvency can take place even in polymer solutions without hydrogen
bonding, since it may be driven by the universal van der Waals and excluded-volume interactions only. The authors established that the microscopic parameter which mainly determines the availability of the co-nonsolvency is the difference between the energetic parameters of polymer–co-solvent and polymer-solvent attraction, i.e., $\epsilon_{pc} - \epsilon_{ps}$. Moreover, they showed that at a sufficiently large value of this difference (or sufficiently low temperature) the coil-globule transition occurs as a first-order phase transition [12,13]. Thus, one can conclude that the co-nonsolvency is a generic physical phenomenon which can be caused by only universal van der Waals and excluded-volume interactions between molecules of the solvent species and monomers [13]. The availability of co-nonsolvency in the mixture N,N dimethylformamide/cyclohexane/polystyrene additionally indicates the correctness of the latter conclusion [19].

Mukherji et al. interpreted the results of their MD simulation by using a simple analytical lattice adsorption model [20,21], taking into account the so-called bridging mechanism which implies that one co-solvent molecule can be strongly associated with two monomers. In other words, from the authors’ point of view the co-nonsolvency usually occurs due to an association of co-solvent molecules with the polymer backbone. It should be noted that within such interpretation “bridging”-induced coil-globule transition is similar to the electrostatically driven coil-globule transition in polyelectrolyte solutions [22–24]. Recently, basing on the full atomistic MD simulation of the PNIPAM chain in mixed water-methanol solvent, a thorough analysis of the entropy and enthalpy contributions to the solvation free energy at the level of linear response approximation for the frozen coil and globule states of polymer chain was provided [18]. The authors showed that in the region of co-nonsolvency, when a collapse of polymer coil takes place the energetics of electrostatic, hydrogen bonding, or bridging-type interactions with the globule is found to play no role. Instead, preferential methanol binding results in a significant increase of the radius of gyration and the local co-solvent mole fraction that confirms earlier results of MD simulations [11–13]. We calculate the solution heat capacity change due to the solvation of polymer chain as a function of the temperature and show that it is in qualitative agreement with the experimental differential scanning calorimetry (DSC) data for PNIPAM in aqueous methanol [9].

**Theory.** — We consider an isolated polymer chain with a degree of polymerization $N_m$ immersed in a low-molecular-weight two-component solvent at a specified number density $\rho$ and temperature $T$ that are located in the fluid state region. So the polymer chain in our model is dissolved in a mixture of solvent and co-solvent which are good ones for the polymer chain. Thus, the co-solvent concentration in the bulk solution is $\rho x$, while the solvent concentration is $\rho (1-x)$, where $x$ is the co-solvent mole fraction in the bulk. Like in recent works [26–29] we assume for convenience that the volume of system consists of two parts: the gyration volume $V_g = 4\pi R_g^3 / 3$ ($R_g$ is the radius of gyration of the polymer chain) containing predominantly monomers of the polymer chain and the bulk solution. To exclude from the consideration the number density change (that can take place near the polymer chain [27,28]) which is unimportant for this research, we assume that the entire polymer solution is incompressible, so that the solvent number density in the gyration volume can be determined by the relation $\rho_1 = \rho - \rho_m$, where $\rho_m = N_m / V_g$ is the monomer number density. Moreover, we introduce a local co-solvent mole fraction $x_1$ by the relations $\rho_s = \rho_1 (1-x_1)$ and $\rho_c = \rho_1 x_1$, where $\rho_s = N_s / V_g$ and $\rho_c = N_c / V_g$ are the local number densities of the solvent and co-solvent in the gyration volume, respectively. We also assume that the pair interaction potentials for monomer-monomer, monomer-solvent, monomer–co-solvent, solvent-solvent, co-solvent–co-solvent, and solvent–co-solvent have a following form:

$$V_{ij}(r) = \begin{cases} -\epsilon_{ij} \left( \frac{\sigma_{ij}}{r} \right)^6, & |r| > \sigma_{ij}, \\ \infty, & |r| \leq \sigma_{ij}, \end{cases}$$

(1)

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where $i,j = m,s,c$; $r = |r|$; $\sigma_{ij}$ and $\epsilon_{ij}$ are effective diameters and energetic parameters, respectively. As in our previous work [28], we assume that $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, whereas each energetic parameter $\epsilon_{ij}$ is considered as independent. Within the present study we do not introduce the second virial coefficients as the parameters of interaction [26,27,30], but as in the work [28] we construct the total free energy by using different expressions which are straightforwardly related to the repulsive and attractive parts of the interaction potentials (1). Moreover, in contrast to the works [26,30] we take into account both solvent species explicitly.

A conditional solvation free energy of the polymer chain can be written as

$$
\Delta G_p(R_g, N_s, N_c) = \mathcal{F}_{id}(R_g, N_s, N_c) + \mathcal{F}_{ex}(R_g, N_s, N_c) + PV_g - \mu_s N_s - \mu_c N_c,
$$

where $R_g$ is the radius of gyration of the polymer chain, $N_s$ and $N_c$ are molecule numbers of the solvent and co-solvent in the gyration volume, respectively: $\mathcal{F}_{id}(R_g, N_s, N_c)$ is the ideal free energy of the polymer chain and mixed solvent which can be calculated in the following way:

$$
\mathcal{F}_{id}(R_g, N_s, N_c) = \frac{9}{4} k_BT \left( \alpha^2 + \frac{1}{\alpha^2} \right) + N_s k_BT \left( \ln \frac{N_s \Lambda_s^3}{V_g} - 1 \right) + N_c k_BT \left( \ln \frac{N_c \Lambda_c^3}{V_g} - 1 \right),
$$

where $\alpha = R_g/R_{0g}$ is the expansion factor, $R_{0g}^2 = N_v b^2/6$ is the mean-square radius of gyration of the ideal Gaussian polymer chain, $b$ is the Kuhn length of the segment, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\Lambda_s$ and $\Lambda_c$ are the de Broglie wavelengths of the solvent species. The first term in (3) is the free energy of the ideal Gaussian polymer chain within the Fixman approximation [31–33]; $P$ is the pressure in the bulk solution which will be determined below. The excess free energy of polymer solution takes the form

$$
\mathcal{F}_{ex}(R_g, N_s, N_c) = \mathcal{F}_{ev}(R_g, N_s, N_c) + \mathcal{F}_{att}(R_g, N_s, N_c),
$$

where $\mathcal{F}_{ex}$ is the contribution of the repulsive interactions in the gyration volume due to the excluded volume of the monomers and molecules of solvent species which we determine through the Mansoori-Carnahan-Starling-Leland equation of state for the hard-spheres mixture (see supporting information Supporting_information.pdf) [34]. The use of the latter equation of state instead the virial equation of state [26,30] allows us to take into account more precisely the packing effects at the large density of solution $\rho$. The contribution of attractive interactions $\mathcal{F}_{att}$ we determine within the standard mean-field approximation as follows:

$$
\mathcal{F}_{att}(R_g, N_s, N_c) = - \sum_{i,j} \frac{N_i N_j a_{ij}}{2 V_g},
$$

where the interaction parameters $a_{ij}$ can be determined by the standard rule:

$$
a_{ij} = \epsilon_{ij} \int_{|r|>\sigma_{ij}} \frac{1}{T} \frac{\sigma_{ij}^3}{\sigma_{ij}^2} \, dr,
$$

where the van der Waals volumes $\epsilon_{ij} = 4\pi \sigma_{ij}^3/3$ are introduced; $i,j = m,s,c$.

We determine the equilibrium values of the expansion factor $\alpha$ and of the local co-solvent mole fraction $x_1$ by the minimization of solvation free energy $\Delta G_p(\alpha, x_1)$ (see supporting information Supporting_information.pdf). It is worth noting that for the practical calculations the local co-solvent mole fraction $x_1$ may be related to the excess coordination number of co-solvent $\Delta N_c = (\rho - \rho_s) V_g$ which is usually used to quantify the stability of given polymer state and describe the preferential binding of co-solvent vs. solvent to the polymer surface in real polymer solutions [35].

**Numerical results and discussions.** – Turning to the numerical calculations, we introduce the dimensionless parameters: $\tilde{T} = k_BT/\epsilon_{ss}$, $\rho = \rho b^3$, $P = P b^3/\epsilon_{ss}$, $\tilde{\epsilon}_{ij} = \epsilon_{ij}/\epsilon_{ss}$, $\tilde{\sigma}_{ij} = \sigma_{ij}/b$. Following the papers of Mukherji et al. [12,13], we use the effective diameters of species: $\tilde{\sigma}_{ss} = \tilde{\sigma}_{cc} = 0.5$, $\tilde{\sigma}_{mm} = 1$. The latter choice approximately corresponds to the PNIPAM chain dissolved in the water-methanol mixed solvent. To get the non-solvency regime, it is needed to take the polymer-co-solvent energetic parameter larger than the other ones. Thus, we choose the following values of the energetic parameters: $\tilde{\epsilon}_{cc} = \tilde{\epsilon}_{ss} = \tilde{\epsilon}_{mm} = 0.5$, $\tilde{\epsilon}_{mc} = 1.5$, so that $\tilde{\epsilon}_{mc} - \tilde{\epsilon}_{ms} = 1$. We also assume that the degree of polymerization of the polymer chain $N_m = 10^4$.

Figures 1(a), (b) illustrate the dependences of the expansion factor $\alpha$ and co-solvent mole fraction $x_1$ in the gyration volume on the bulk co-solvent mole fraction $x$ at different values of temperature $\tilde{T}$ under the fixed pressure $P = 0.35$. As is seen, at sufficiently high temperature at increasing co-solvent mole fraction $x$ the reentrant coil-to-globule-to-coil transition proceeds smoothly, while the co-solvent mole fraction $x_1$ in the gyration volume monotonically increases. However, when the temperature drops below a certain threshold value, the polymer chain undergoes the coil-globule transition in a regime of first-order phase transition. Namely, when the discontinuous decrease in the expansion factor takes place, the local mole fraction of co-solvent in the gyration volume simultaneously abruptly increases. At further increase in the mole fraction of co-solvent in the bulk solution, the expansion factor and the mole fraction of co-solvent in the gyration volume smoothly increase. It is worth noting that the increase in the temperature leads to the shift of the threshold co-solvent mole fraction at which the coil-globule transition takes place to higher values. This trend qualitatively agrees with the results of the both experiment and MD computer simulation [4]. We would also like to stress
Fig. 1: (Colour online) The dependences of expansion factor $\alpha$ (a) and local co-solvent mole fraction $x_1$ (b) on the co-solvent mole fraction $x$ in the bulk solution under the fixed pressure $\tilde{P} = 0.35$ at different values of temperature $\tilde{T}$. A sufficiently high temperature at increasing co-solvent mole fraction $x$, the reentrant coil-to-globule-to-coil transition proceeds smoothly, while the co-solvent mole fraction $x_1$ in the gyration volume monotonically increases. However, when the temperature drops below a certain threshold value, the polymer chain undergoes the coil-globule transition in a regime of first-order phase transition. Namely, when the discontinuous decrease of the expansion factor takes place, the local mole fraction of co-solvent in the gyration volume abruptly increases.

that the availability of the region where the increase in bulk co-solvent mole fraction has only minor effect on the local solvent/co-solvent composition is a natural consequence of the co-solvent molecules’ preferential binding with the polymer backbone. Indeed, in the case of strong attractive interactions between polymer and co-solvent, the co-solvent–induced coil-globule transition is accompanied by a significant increase of the co-solvent concentration within the polymer volume [24,26,30]. So when the polymer chain adopts a compact globular conformation, further increase in the bulk co-solvent mole fraction should lead only to minor increase in the local co-solvent concentration due to excluded-volume effects. Moreover, the above-mentioned behavior of the local co-solvent mole fraction is in qualitative agreement with the results of MD simulations of conformation transition of PNIPAM hydrogel as a function of the methanol mole fraction in water/methanol mixtures [4].

As already pointed out above, the abrupt increase in the local co-solvent mole fraction additionally confirms the results of works [24,26,30] that in the case of strong polymer–co-solvent attraction the co-solvent molecules must be enriched in the globule. Nevertheless, an implicit accounting for the solvent molecules does not allow us to obtain the reentrant coil-to-globule-to-coil transition, but only co-solvent–induced coil-globule transition [26,30]. In our opinion, it may be related to the fact that implicit solvent models do not take into account the preferential binding co-solvent vs. solvent to the polymer chain which, it seems, should play a crucial role in the co-nonsolvency. Moreover, the presence of an abrupt decrease in the expansion factor predicted by the present theory confirms the earlier MD simulations results [11–13]. Finally before we pass to the discussion of the thermodynamic aspects of the co-nonsolvency, it is instructive to discuss how the difference between the energetic parameters of attraction polymer–co-solvent and polymer-solvent, $\epsilon_{mc} - \epsilon_{ms}$, influences the coil-to-globule-to-coil transition. We obtain (see fig. 2) that the increase in the difference $\epsilon_{mc} - \epsilon_{ms}$ leads to a more pronounced coil-to-globule-to-coil transition that also confirms the recent MD simulations results [12,13]. It should be noted that the increase in the degree of polymerization $N_m$ also leads to a more pronounced coil-to-globule-to-coil transition.

In order to understand the thermodynamic nature of co-nonsolvency, we discuss the behavior of entropic and enthalpic contributions to the solvation free energy of the polymer chain in the region where the reentrant coil-to-globule-to-coil transition takes place. We shall discuss below the solvation free energy per monomer $\Delta G_p/N = \Delta g_p = \Delta h_p - T\Delta s_p$, where $\Delta s_p = -\partial \Delta g_p/\partial T$ and $\Delta h_p = -T^2 \partial^2 \Delta g_p/\partial T^2$ are the entropy and enthalpy
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Fig. 3: (Colour online) The dependences of the free energy $\Delta \tilde{g}_p$ (black lines), the enthalpy $\Delta \tilde{h}_p$ (blue lines), and the entropy $-\tilde{T}\Delta \tilde{s}_p$ (red lines) of solvation per monomer expressed in units of $\epsilon_{ss}$ on the co-solvent mole fraction $x$ in the bulk solution at the fixed pressure $\tilde{P} = 0.35$ and the temperatures (a) $\tilde{T} = 0.4$ and (b) $\tilde{T} = 0.38$. Enthalpy $\Delta h_p$ and entropy $-\tilde{T}\Delta s_p$ contributions are strongly oscillating functions of the co-solvent mole fraction $x$ in the region of co-nonsolvency in both cases. The entropy and enthalpy contributions to the solvation free energy almost compensate each other.

Fig. 4: (Colour online) The solution heat capacity change $\Delta \tilde{C}_p = \partial \Delta \tilde{H}/\partial \tilde{T}$ due to the polymer chain solvation as a function of temperature $\tilde{T}$ at different solvent composition $x$. Each curve $\Delta \tilde{C}_p = \Delta C_p/k_B$ has pronounced minimum which decreases with increase in the bulk co-solvent mole fraction $x$. Such behavior of $\Delta \tilde{C}_p$ is in qualitative agreement with the experimental data on the heat flow of PNIPAM in aqueous methanol obtained by the differential scanning calorimetry (DSC) method [9]. The data are shown for $\tilde{T} = 0.4$, $\tilde{P} = 0.35$, $\epsilon_{ms} = 0.5$, $\epsilon_{mc} = 1.5$.

Conclusion. – Taking into account the effects of conformational entropy, renormalizing the solvent composition near the polymer backbone, and universal intermolecular excluded-volume and van der Waals interactions within the self-consistent field theory, we have described the reentrant coil-to-globule-to-coil transition of a polymer chain in a mixture of good solvents. We show that, when the collapse of the polymer chain takes place, the entropy and enthalpy contributions to the solvation free energy of the globule strongly grow almost compensating each other. From the first principles of statistical thermodynamics we confirm earlier speculations based on the MD simulations results that the co-nonsolvency is regime of first-order phase transition. In contrast to the enthalpy and entropy of solvation, the free energy of solvation in the co-nonsolvency region is close to zero. The latter means that the entropy and enthalpy contributions almost compensate each other. Thus the co-nonsolvency has to be considered as a complex thermodynamic process driven by entropy-enthalpy compensation that confirms the speculations presented in works [12,13]. It is interesting to discuss the change of solution heat capacity $\Delta C_p = \partial \Delta H_p/\partial T$ due to the polymer chain solvation as a function of the temperature at different solvent composition $x$ in the co-nonsolvency region. We obtain (see fig. 4) that each curve $\Delta \tilde{C}_p = \Delta C_p/k_B$ has a pronounced minimum which decreases with increase in the bulk co-solvent mole fraction $x$. Such behavior of $\Delta \tilde{C}_p$ is in qualitative agreement with the experimental data on the heat flow of PNIPAM in aqueous methanol obtained by the differential scanning calorimetry (DSC) method [9].

of solvation per monomer, respectively. In figs. 3(a), (b) are depicted the dependences of solvation entropy and solvation enthalpy on the co-solvent mole fraction at the fixed pressure $\tilde{P} = 0.35$ and the temperatures (a) $\tilde{T} = 0.4$ and (b) $\tilde{T} = 0.38$. Enthalpy $\Delta h_p$ and entropy $-\tilde{T}\Delta s_p$ contributions are strongly oscillating functions of the co-solvent mole fraction $x$ within the region of co-nonsolvency in both cases. The entropy and enthalpy contributions to the solvation free energy almost compensate each other.
the essentially enthalpic-entropic effect and is caused by enthalpy-entropy compensation.

However, we would like to discuss the limitations of the present self-consistent field theory. First, in this work we use the unrealistic potentials of interaction between the particles of the solution. In order to apply this theory to real polymer solutions, one can take the more realistic Lennard-Jones potentials using the standard Weeks-Chandler-Andersen procedure [36]. However, in the present work we have demonstrated only the principle possibility to describe the co-nonsolvency within self-consistent field theory, retaining its application to the experimental systems for the future researches. Second, our theory in the present form is based on the assumption that the entire polymer solution is incompressible. Such approximation must be invalid in the region of extremely high pressures [27]. Recently it was experimentally observed [7] and confirmed by full atomistic MD simulations [14] that the co-nonsolvency of PNIPAM in aqueous methanol can be suppressed by application of sufficiently high pressure (order of 500 MPa). To describe this very interesting phenomenon theoretically it is necessary to go beyond the incompressibility approximation that is a subject of forthcoming publications.

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