# Unified View on the Mean-Field Order of Coil–Globule Transition

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ABSTRACT: It is concluded that the mean-field coil–globule transition of a polymer chain of finite length N immersed in a small-molecule solvent exhibits the type-I behavior; that is, it is either a first-order phase transition, a critical point, or a crossover depending on the location of the critical point. It becomes a second-order phase transition with respect to the solvent equality characterized by the Flory–Huggins parameter χ (or equivalently the second virial coefficient v or the temperature T) only in the limit of $N \to \infty$. Even in this limit, it still has the type-I behavior with respect to $vN^{1/2}$ (or equivalently $(1 - 2\chi)N^{1/2}$).
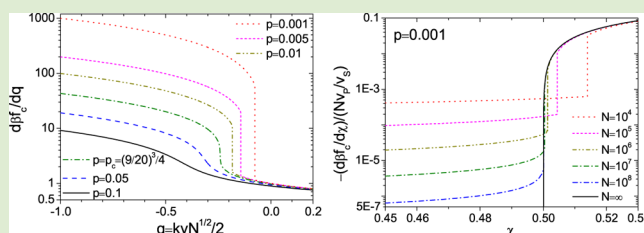
It is well-known that a polymer chain immersed in a small-molecule solvent undergoes the coil–globule transition (CGT) between the expanded (coil) and collapsed (globule) states as the solvent quality changes, which has been the subject of extensive research.[1,2] In the study of CGT, a mean-field theory, either of the Flory-type[3–12] or the self-consistent field theory,[13,14] has been commonly used; the transition order predicted by the mean-field theory, however, has been controversial. For example, in refs 3–9 and 13 it is predicted to be either a first-order phase transition, a critical point, or a crossover (similar to the condensation of simple liquids) depending on the chain stiffness, while in refs 10, 11, and 14 it is predicted to be a second-order phase transition. In this Letter we clarify the mean-field behavior of CGT and resolve the controversy on its transition order.

Let us consider the Flory-type Helmholtz free energy f_c of a single chain with N segments in a poor solvent given by

$$\beta f_c = \frac{3}{2}\alpha^2 - 3 \ln \alpha + \frac{1}{2}va^3 N\overline{\rho} + \frac{1}{6}\omega a^6 N\overline{\rho}^2 \quad (1)$$

which was first used by Ptitsyn and Eizner[3] to investigate CGT and was further developed in refs 4 and 5 and by other researchers.[6–13] In eq 1, $\beta \equiv 1/k_B T$, with k_B being the Boltzmann constant and T is the thermodynamic temperature; the first two terms on its right-hand side represent the elastic free energy of the chain, where $\alpha \equiv (R_e^2/R_{e,0}^2)^{1/2}$ is the chain expansion factor with R_e^2 and $R_{e,0}^2 = Na^2$ being the mean-square end-to-end distance of the real chain and that of an ideal chain, respectively, and a is the statistical segment length; and the last two terms represent the polymer–solvent interaction energy, where v and ω are the second and third virial coefficients, respectively, and $\overline{\rho} \equiv N/V_c$ is the average number density of polymer segments within the chain volume $V_c = R_e^3/k$ with k being a numerical constant (e.g., $k = 6/\pi$). With $\overline{\rho}a^3 = kN^{-1/2}\alpha^{-3}$, eq 1 can be rewritten as

$$\beta f_c = \frac{3}{2}\alpha^2 - 3 \ln \alpha + \frac{1}{2}kvN^{1/2}\alpha^{-3} + \frac{1}{6}k^2\omega\alpha^{-6} \quad (2)$$

Minimizing βf_c with respect to α gives

$$\alpha^5 - \alpha^3 - \frac{p}{\alpha^3} = q \quad (3)$$

where $p \equiv k^2\omega/3$ and $q \equiv kvN^{1/2}/2$.

Note that eq 3 exhibits similar behavior to a cubic equation of state (in terms of α^3); that is, for $p > p_c = (9/20)^3/4$ the value of α continuously and monotonically increases with increasing q (or equivalently $vN^{1/2}$), and for $0 < p < p_c$ three different values of α can be found at given $q > q_c = -(4/5)(9/20)^{3/2}$. This behavior of α is regardless of the value of N (including the limit of $N \to \infty$), and has been reported in many studies.[3–9,13] Here we examine the first- and second-order derivatives of βf_c with respect to q, the continuity of which *defines* the transition order[15] of CGT but has not been reported in the literature. Substituting eq 3 into eq 2, we obtain the minimized βf_c as

$$\beta f_c = \frac{5}{2}\alpha^2 - 3 \ln \alpha - 1 - \frac{1}{2}p\alpha^{-6} \quad (4)$$

At given p, the above gives $d\beta f_c/d\alpha = 5\alpha - 3\alpha^{-1} + 3p\alpha^{-7}$ and eq 3 gives $dq/d\alpha = 5\alpha^4 - 3\alpha^2 + 3p\alpha^{-4}$. We then have

$$\frac{d\beta f_c}{dq} = \frac{d\beta f_c}{d\alpha}\frac{d\alpha}{dq} = \frac{1}{\alpha^3(p, q)} \quad (5)$$

$$\frac{d^2\beta f_c}{dq^2} = \frac{d}{d\alpha}\left(\frac{d\beta f_c}{dq}\right)\frac{d\alpha}{dq} = -\frac{1}{5\alpha^8(p, q)/3 - \alpha^6(p, q) + p} \quad (6)$$
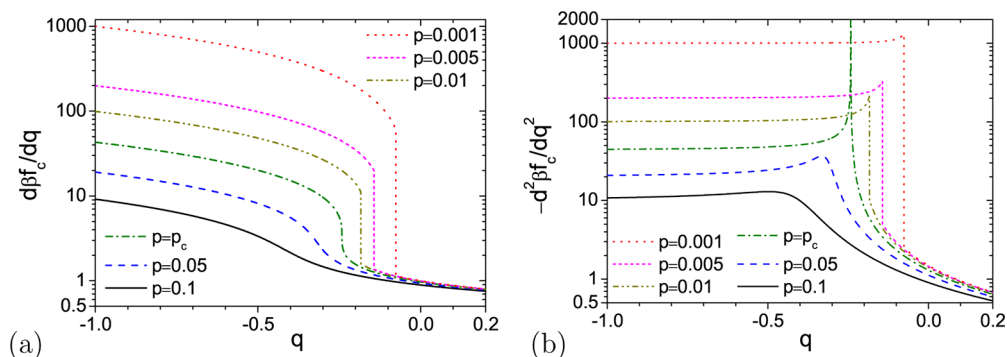
with $\alpha(p,q)$ given by eq 3.

Figure 1 clearly shows that for $p < p_c$, $d\beta f_c/dq$ (and $d^2\beta f_c/dq^2$) exhibits a discontinuity (due to the existence of two different α-values) at $q > q_c$, indicating that CGT is a first-order phase transition; at $p = p_c$, $d\beta f_c/dq$ is continuous but $d^2\beta f_c/dq^2$ diverges at $q = q_c$, indicating a critical point; and for $p > p_c$, both
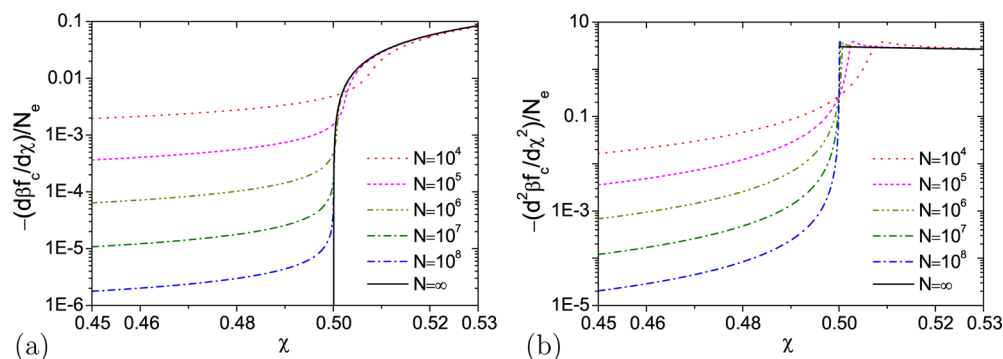
Figure 1. Semilogarithmic plots of (a) the first- and (b) the second-order derivatives of βf_c with respect to q at various p, given by eqs 5 and 6, respectively.

Figure 2. Semilogarithmic plots of (a) the first- and (b) the second-order derivatives of βf_c with respect to χ at various N, given by eqs 12 and 13, respectively. Note that in the limit of $N \to \infty$ both the derivatives divided by N_e are 0 for $\chi < 1/2$, and that $p = 0.1$ and $r_s = 1$ are used here.

derivatives are continuous, indicating a "crossover" (termed for our purpose; strictly speaking, one needs to prove that all higher-order derivatives are continuous). This behavior of CGT is referred to as "type-I" hereafter.

Equation 1 is for an implicit solvent. One can also consider an explicit solvent, where βf_c is given by[3−5,7]

$$\beta f_c = \frac{3}{2}\alpha^2 - 3 \ln \alpha + n_S \ln(1 - \phi_p) + \chi n_S \phi_p \quad (7)$$

Here $\phi_P \equiv v_P \bar{\rho}$ and $n_S \equiv (1 - \phi_p)V_c/v_S$ are the average polymer volume fraction and the number of solvent molecules within the volume V_c, respectively, with v_P and v_S being the volume of each polymer segment and solvent molecule, respectively, and χ is the Flory–Huggins interaction parameter between a polymer segment and a solvent molecule. Defining $r_f \equiv v_P/a^3$, which measures the chain stiffness, and $r_s \equiv v_P/v_S$, which measures the size ratio between a polymer segment and a solvent molecule, and Taylor-expanding $\ln(1 - \phi_p)$ to the third order in ϕ_P, we have

$$\beta f_c \approx \frac{3}{2}\alpha^2 - 3 \ln \alpha + \frac{1}{2}kr_s r_f (1 - 2\chi)N^{1/2}\alpha^{-3} + \frac{1}{6}k^2 r_s r_f^2 \alpha^{-6} \quad (8)$$

where an unimportant constant is omitted. Comparing eq 8 to eq 1, we find $v = (1 - 2\chi)r_s r_f$ and $\omega = r_s r_f^2$.

While the above expansion of $\ln(1 - \phi_p)$ is only valid for $\phi_P \ll 1$ (i.e., large N in the coil and θ states) with higher-order terms needed when $\phi_P \sim O(1)$, it does not qualitatively change the type-I behavior of CGT, but only changes the exact location of the critical point.[3,4,10] Similarly, using either a more accurate

expression of the elastic free energy,[8,9,12] a Gaussian (instead of uniform) distribution of polymer segments in V_c,[5,7] or the expansion factor based on the chain radius of gyration,[5,8,9,12] as well as varying r_s[5] or r_f[3−5,7,13] do not qualitatively change the type-I behavior of CGT.

On the other hand, in the limit of $N \to \infty$, Moore,[14] Sanchez,[10] and Di Marzio[11] concluded that CGT is a second-order phase transition with respect to T (or equivalently v or χ). In particular, Sanchez[10] pointed out that, because α of the coil state diverges in the limit of $N \to \infty$, it is better to use ϕ_P, which is bounded for all N, as an order parameter for CGT. Replacing α^3 by ϕ_0/ϕ_P, where ϕ_0 is the corresponding value of ϕ_P in the θ solvent (i.e., where $\alpha = 1$), we obtain from eq 7

$$\beta f_c = \frac{3}{2}\left(\frac{\phi_0}{\phi_P}\right)^{2/3} - \ln \frac{\phi_0}{\phi_P} + N_e \frac{1 - \phi_P}{\phi_P}\ln(1 - \phi_p) - N_e \chi \phi_P \quad (9)$$

where $N_e \equiv r_s N$ is the effective chain length taking into account the size ratio between a polymer segment and a solvent molecule, and an unimportant constant is omitted. Note that, with $r_s = 1/2$ and $\chi = \theta/2T$, where θ denotes the θ temperature, eq 9 reduces to the free-energy expression used by Sanchez (i.e., eq 25b in ref 10), with the only difference being that the coefficient 3/2 in our eq 9 is replaced by 7/2, which does not qualitatively change the phase behavior of CGT. At given χ, minimizing βf_c with respect to ϕ_P gives

$$\frac{1}{N_e} - 1 - \frac{1}{N_e}\left(\frac{\phi_0}{\phi_P}\right)^{2/3} - \frac{\ln(1 - \phi_p)}{\phi_P} = \chi \phi_P \quad (10)$$
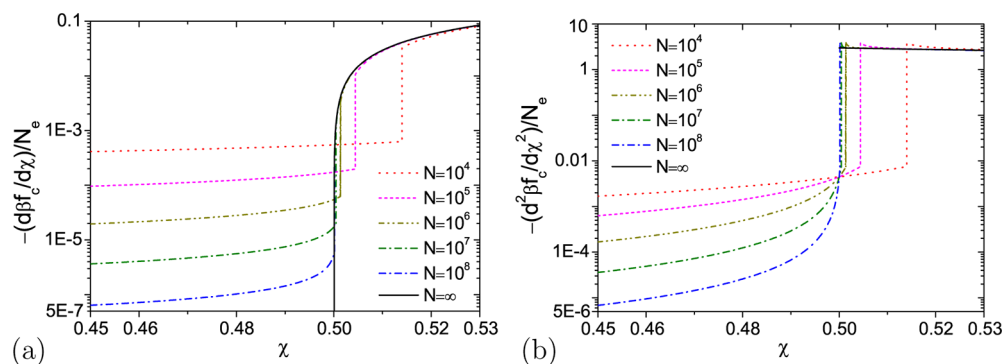
Figure 3. Same as Figure 2 but with $p = 0.001$.

and the minimized free energy

$$\beta f_c = \frac{5}{2}\left(\frac{\phi_0}{\phi_P}\right)^{2/3} - \ln\frac{\phi_0}{\phi_P} + N_e\frac{2 - \phi_P}{\phi_P}\ln(1 - \phi_P) + N_e$$
$$- 1. \tag{11}$$

The first- and second-order derivatives of βf_c with respect to χ are then obtained as

$$\frac{d\beta f_c}{d\chi} = \frac{d\beta f_c}{d\phi_P}\frac{d\phi_P}{d\chi} = -N_e\phi_P(\chi, \phi_0, N_e) \tag{12}$$

$$\frac{d^2\beta f_c}{d\chi^2} = \frac{d}{d\phi_P}\left(\frac{d\beta f_c}{d\chi}\right)\frac{d\phi_P}{d\chi}$$
$$= \frac{-3N_e\phi_P^2}{2/N_e - 2 - 5\chi\phi_P + \ln(1 - \phi_P)/\phi_P + 3/(1 - \phi_P)} \tag{13}$$

with $\phi_P(\chi, \phi_0, N_e)$ given by eq 10.

Figure 2 shows $d\beta f_c/d\chi$ and $d^2\beta f_c/d\chi^2$ for various N at $p = \phi_0^2 N_e/3 = 0.1 > p_c$ (thus, in the crossover region predicted by eq 2), where $r_s = 1$ is used. We find that $d\beta f_c/d\chi$ is continuous for all N, and that $d^2\beta f_c/d\chi^2$ is continuous for all finite N but exhibits a discontinuity at $\chi = 1/2$ in the limit of $N \to \infty$. In this limit (denoted by the superscript "∞" hereafter), we note that $\phi_P \to 0$ in both the coil and θ states, and that ϕ_P is independent of N in the globule state but is small just below the θ temperature. Taylor-expanding $\ln(1 - \phi_P)$ in eq 10 to the fourth order in ϕ_P, which is valid near the θ temperature, then gives $\chi \approx -(1/N_e\phi_P)(\phi_0/\phi_P)^{2/3} + 1/2 + \phi_P/3 + \phi_P^2/4$. Because $(1/N_e\phi_P)(\phi_0/\phi_P)^{2/3} = (kr_f/r_s)\phi_P^{-5/3}N^{-4/3} \to 0$ in the globule (G) state, we obtain $\phi_{P,G}^{\infty} = (2/3)((9\chi - 7/2)^{1/2} - 1)$ just below the θ temperature and can write $\phi_P^{\infty} = \phi_{P,G}^{\infty}H(\chi - 1/2)$ with $H(x)$ denoting the Heaviside step function. Finally, eqs 12 and 13 give, respectively, $-(d\beta f_c/d\chi)^{\infty}/N_e = \phi_P^{\infty}$, which is continuous at $\chi = 1/2$, and $-(d^2\beta f_c/d\chi^2)^{\infty}/N_e = 3(9\chi - 7/2)^{-1/2}H(\chi - 1/2)$, which is discontinuous at $\chi = 1/2$. Our analysis here is supported by the fact that the numerical results of $d\beta f_c/d\chi$ and $d^2\beta f_c/d\chi^2$ approach these limiting values with increasing N, as shown in both Figures 2 and 3. For the case shown in Figure 2, CGT is therefore a crossover for finite N but becomes a second-order phase transition with respect to χ only in the limit of $N \to \infty$.

Figure 3 shows $d\beta f_c/d\chi$ and $d^2\beta f_c/d\chi^2$ for various N at $p = 0.001 < p_c$ (thus, in the first-order transition region predicted by eq 2), where $r_s = 1$ is used. We see that $d\beta f_c/d\chi$ exhibits a

discontinuity for all finite N but becomes continuous in the limit of $N \to \infty$, and that $d^2\beta f_c/d\chi^2$ is discontinuous for all N.

We therefore conclude that CGT has the type-I behavior for finite N, and only in the limit of $N \to \infty$ becomes a second-order phase transition with respect to χ. Note that, even in this limit, CGT still has the type-I behavior with respect to $vN^{1/2}$ (or equivalently $(1 - 2\chi)N^{1/2}$).

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Notes
The authors declare no competing financial interest.

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