Mean-Field Theory on Temperature-Concentration Diagram of Polymer Solutions

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ABSTRACT: The temperature-concentration diagram of polymer solutions was studied by application of the mean-field theory on the basis of certain simple assumptions. In concentrated solutions, it was assumed that the excluded-volume effect decreases proportionally with C_R/C , where C_R is the concentration of segments belonging to the assigned chain in its sphere and C is the macroscopic segment concentration. The mean-square radius, cross-over line, osmotic pressure, and correlation length were derived for each of Regions I, I', II, III, and IV defined by Daoud and Jannink. These results fully agreed with those obtained by the scaling laws.

KEY WORDS Mean-Field Theory / Excluded-Volume Effect / Concentrated Solution / Mean-Square Radius / Cross-Over Line / Osmotic Pressure / Correlation Length /

Daoud and Jannink¹ (DJ) derived the temperature-concentration diagram of polymer solutions. A magnetic analogue and the scaling laws were used for the derivation of the diagram. In another paper,² DJ *et al.* gave more intuitive derivations and pointed out the deviation from the mean-field theory in semidilute solutions.

Recent experimental results, especially by neutron scattering,² seem to support more the relationships derived by the scaling laws than those derived by the mean-field theory. This means that assumptions used in the mean-field theory up to the present are not applicable to semidilute solutions. The purpose of this paper is an attempt to reconcile these two different methods on the basis of certain simple assumptions.

ASSUMPTIONS

A polymer chain is assumed to be a sphere of radius R in which N segments (N , the number of segments per chain) are uniformly distributed. The distribution function $W(R)$ is assumed to be as follows.

$$W(R) = W_0(N, R) \cdot P(N, R, \beta_i, C) \quad (1)$$

$$W_0(R) \sim R^2 N^{-3/2} \exp \{-(R^2/b^2 N)\} \quad (2)$$

$$P(N, R, \beta_i, C) \sim \exp \{ -[\sum \beta_i (N/R^3)^i v(C)] \} \quad (3)$$

where β_i is the i th virial coefficient of the segments, $C (\equiv NN_p/V, N_p$; the number of polymer chains in the solution) is the segment concentration, b is the segment length and $v(C)$ is the effective volume which contributes to the excluded-volume effect in a chain sphere at concentration C (see the following). We also define the polymer concentration as $C_p \equiv N_p/V$ and the segment concentration of the appointed chain in its chain sphere as $C_R \equiv N/R^3$. In eq 3, $(N/R^3)^i$ is a measure of the probability of i -segments contact and $Z_i \equiv (N/R^3)^i v(C)$ gives the average number of effective i -segments contacts.³

$W_0(N, R)$ represents the gaussian character of the unperturbed state and $P(N, R, \beta_i, C)$ is the perturbation term. Since $-kT \ln W(R)$ corresponds to the Landau free energy in phase transitions, equilibrium properties are determined by the minimum of $-kT \ln W(R)$ with respect to the order parameter R .

Similarly to well known facts in imperfect gases,³ it is assumed that near the Θ temperature, β_2 is proportional to $\tau = (T - \Theta)/\Theta$ (Θ is the temperature of $\beta_2 = 0$) and β_3 is positive and nearly constant. Therefore, the τ dependence is equivalent to the β_2 dependence.

The effective volume $v(C)$ is assumed as,

$$v(C \ll C^*) = R^3 \quad (4) \quad \text{and}$$

and

$$v(C \gg C^*) = R^3(C_R/C) = N/C = 1/C_p \quad (5)$$

where C^* is the cross-over concentration between Regions I and II defined by DJ. Equation 5 is a new and basic assumption proposed in this paper for semidilute solutions. The above equation represents the decrease in the effective volume by the increase in concentration, or in other words, by segments of other polymer chains. The 2nd and 3rd equalities in eq 5 show that the effective volume in semidilute solutions is dependent only on the concentration (C^{-1} per segment and C_p^{-1} per polymer chain) and is independent of the radius R . On the other hand, the effective volume in dilute solutions, eq 4, is the volume of the chain sphere R^3 per polymer (R^3/N per segment) itself.

The intuitive interpretation of eq 5 is as follows. In $C \gg C^*$ solutions, segments of other polymers penetrate the chain sphere. The average concentration of penetrated segments in the chain sphere is assumed to be equal to the macroscopic concentration C . The number of the contacts among a segment belonging to the assigned chain and i penetrated segments in the chain sphere is proportional to $C^i C_R R^3$, which is independent of the chain radius R . The excluded-volume effect is caused only by contacts among segments of the chain. Contacts with penetrated segments merely uniformly depress the original gaussian distribution $W_0(R)$. Since penetrated segments hinder contacts among segments of the assigned chain, the excluded-volume effect decreases. This decrease is represented as a decrease in the effective volume $v(C)$. The simplest measure of this effect is approximated by C_R/C , which is the probability finding the segment of the assigned chain from among segments in the chain sphere. As a result, the 2nd and 3rd equalities are derived; these equalities mean that the effective volume per segment is the same as the average volume of penetrated segments. The segments are uniformly distributed in $C \gg C^*$ solutions on the average. The above is essentially a revival of the Flory approximation.

The average number of effective i -segments contacts Z_i is given by eq 3—5 as follows.

$$Z_i(C \ll C^*) \sim N^i/R^{(i-1)} \quad (6)$$

$$Z_i(C \gg C^*) \sim (N^{i+1}/R^{3i})(1/C) \quad (7)$$

If R is represented by $\sim N^\nu$, Z_i 's to be considered are as follows. When $\nu > 1/2$, Z_i 's ($i > 2$) are negligible as $N \rightarrow \infty$. When $\nu = 1/2$, $Z_i(C \ll C^*)$'s ($i > 3$) and $Z_i(C \gg C^*)$'s ($i > 2$) are negligible as $N \rightarrow \infty$. As ν decreases below $1/2$, higher Z_i 's are required and when $\nu = 1/3$, all Z_i 's become relevant ($\sim N$), in eq 3.

In the following sections, Regions I ~ IV, defined by DJ, are interpreted as follows.

Region I — above Θ dilute region —

$$\beta_2 > 0, \beta_3 > 0 \text{ and } C < C^* \text{ region,}$$

Region I' — Θ region —

$$\beta_2 = 0, \beta_3 > 0 \text{ and } C < C^* \text{ region,}$$

Region II — semidilute region —

$$\beta_2 > 0 \text{ } (\beta_3 > 0) \text{ and } C^* < C < C^{**} \text{ region,}$$

Region III — concentrated tricritical region —

$$\beta_2 = 0 \text{ } (\beta_3 > 0) \text{ and } C > C^{**} \text{ region,}$$

Region IV — below Θ dilute region —

$$\beta_2 < 0, \beta_3 > 0 \text{ and } C < C_{\text{crit}} \text{ region,}$$

where C^* and C^{**} are the cross-over concentrations between Regions I, II, and II, III, respectively, and C_{crit} is the critical concentration of phase separation.

MEAN-SQUARE RADIUS $\langle R^2 \rangle$

Using eq 1—3 and 5, along with the minimization of the function $-kT \ln W(R)$, the following equations are obtained for the Flory's expansion factor α ,

$$\alpha^5 - \alpha^3 \sim \beta_2 N^{1/2} + \beta_3 \alpha^{-3} \quad (\text{for Regions I, I', and IV}) \quad (8)$$

$$\alpha^8 - \alpha^6 \sim (\beta_2/C) \quad (\text{for Regions II and III}) \quad (9)$$

$\langle R^2 \rangle$ of each region is given as follows as $N \rightarrow \infty$:

$$\text{Region I } \langle R^2 \rangle \sim \beta_2^{2/5} N^{6/5} \sim \tau^{2/5} N^{6/5} \quad (10)$$

$$\text{Region I' } \langle R^2 \rangle \sim (1 + \beta_3)N \sim N \quad (11)$$

$$\text{Region II } \langle R^2 \rangle \sim \beta_2^{1/4} C^{-1/4} N \sim \tau^{1/4} C^{-1/4} N \quad (12)$$

$$\text{Region III } \langle R^2 \rangle \sim N \sim N \quad (13)$$

$$\text{Region IV } \langle R^2 \rangle \sim (-\beta_3/\beta_2)^{2/3} N^{2/3} \sim -\tau^{-2/3} N^{-2/3} \quad (14)$$

These results are consistent with those of DJ.

Equation 8 is the same as the equation derived earlier by Ptitsyn *et al.*⁴, and was recently reviewed by de Gennes.⁵ From eq 3, 8, and 11, it is obvious in the θ -region that although $\langle R^2 \rangle \sim N$, the distribution function $W(R)$ is not gaussian, since the β_3 term is relevant as already pointed out in a previous paper.³ Equation 14 derived from eq 8 predicts the collapse of a chain as first shown by Ptitsyn.⁴ However, this prediction is incomplete, since all terms in eq 3 become relevant in the same order ($\sim \beta_i N$) at $v=1/3$. Thus eq 14 agrees formally with the result from the scaling laws, but further study is needed for making a complete interpretation by the mean-field theory.

The mean-field theoretic derivation of eq 9 was first mentioned in this paper using the assumption of eq 5. In Regions II and III, the terms including β_i ($i>2$) in eq 3 are negligible as $N \rightarrow \infty$ and the expansion factors α are not dependent on N . The distribution function $W(R)$ of Region III is gaussian for the whole range of R and $W(R)$ of Region II is gaussian near the maximum ($R^2 \sim N$).

CROSS-OVER LINE

The cross-over lines between each region are obtained from the relations $\langle R^2 \rangle$ (Region A) $\sim \langle R^2 \rangle$ (Region B). The results are as follows:

$$\text{Region I} \sim \text{Region I}' \quad |\tau| \sim N^{-1/2} \quad (15)$$

$$\text{Region I} \sim \text{Region II} \quad C^* \sim \tau^{-3/5} N^{-4/5} \quad (16)$$

$$\text{Region II} \sim \text{Region III} \quad C^{**} \sim \tau \quad (17)$$

These results also agree with those of DJ.

OSMOTIC PRESSURE Π

It is a matter of course from thermodynamic considerations that π/T is proportional to C/N in dilute regions—Regions I, I', and IV. The second term of π/T in the virial expansion is represented by $A_2 C^2$ and it is known that A_2 is proportional to $\langle R^2 \rangle^{3/2}/N^2$ in dilute regions.² The latter quantity is rewritten to $\langle Z_2(C \ll C^*)^{-1} \rangle$ by eq 6. Z_2^{-1} is considered to be the effective hard core volume for intermolecular segment contacts. Expanding this consideration to Regions II and III—and neglecting the first term C/N —, π/T becomes $\langle Z_2(C \gg C^{**})^{-1} \rangle C^2 = \langle R^6 C/N^3 \rangle C^2$. Using eq 12 and 13 for R , next relations are derived,

$$\text{Region I, I', and IV} \quad \pi/T \sim C/N \quad (18)$$

$$\text{Region II} \quad \pi/T \sim \tau^{3/4} C^{9/4} \quad (19)$$

$$\text{Region III} \quad \pi/T \sim C^3 \quad (20)$$

These relationships agree with those of DJ.

CORRELATION LENGTH ξ

All segments in an isolated chain correlate to each other. Therefore the correlation volume ξ^3 is $\langle R^2 \rangle^{3/2}$ in dilute regions. In Regions II and III, the number of segment contacts is proportional to π/T^1 and the correlation volume ξ^3 is proportional to the inverse of this number. The correlation length in each region is given as follows.

$$\text{Region I} \quad \xi^2 \sim \tau^{2/5} N^{6/5} \quad (21)$$

$$\text{Region I}' \quad \xi^2 \sim N \quad (22)$$

$$\text{Region II} \quad \xi^2 \sim \tau^{-1/2} C^{-3/2} \quad (23)$$

$$\text{Region III} \quad \xi^2 \sim C^{-2} \quad (24)$$

$$\text{Region IV} \quad \xi^2 \sim -\tau^{-2/3} N^{2/3} \quad (25)$$

These relationships also agree with those of DJ. However, as mentioned in the section of $\langle R^2 \rangle$, further study is needed for Region IV.

CONCLUSION

The relationships obtained here were fully coincided with the results derived by DJ using the scaling laws. In the derivation in this paper, the basic assumption involved in eq 5 is essential. At this stage, use of this assumption was intuitive; its physical basis is somewhat obscure. Further study is needed for reconciling the mean-field theory with the scaling laws.

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