SCALING AND CROSSOVER TO TRICRITICALITY IN POLYMER SOLUTIONS

M.A.Anisimov[+], V.A.Agayan[+], E.E.Gorodetskii[+*]

[+]Institute for Physical Science and Technology and Department of
Chemical Engineering, University of Maryland
College Park, MD 20742, U.S.A.

[*]Oil and Gas Research Institute RAS
117971 Moscow, Russia

We propose a scaling description of phase separation of polymer solutions. The scaling incorporates three universal limiting regimes: the Ising limit asymptotically close to the critical point of phase separation, the "ideal gas" limit for the pure-solvent phase, and the tricritical limit for the polymer-rich phase asymptotically close to the *theta* point. We have also developed a phenomenological crossover theory based on the near-tricritical-point Landau expansion renormalized by fluctuations. This theory validates the proposed scaled representation of experimental data and crossover to tricriticality.

PACS: 05.70.Jk, 42.70.Jk, 64.75.+g,

Phase separation in solutions of polymers in low-molecular-weight (monomer-like) solvents changes dramatically with increase of the degree of polymerization (Fig.1) [1]. Like in simple binary liquids, asymptotically close to the critical point the coexistence curves obey a universal power law of the form

$$\phi - \phi_c = \pm B_0 \left| \tau \right|^{\beta}, \tag{1}$$

where ϕ is the volume fraction of polymer, ϕ_c is the critical volume fraction; $\tau = (T - T_c)/T$, T is the temperature, T_c is the critical temperature; $\beta = 0.326 \pm 0.001$ is a universal 3-dimensional (3D) Ising critical exponent [2], B_0 is a system-dependent critical amplitude. However, with increase of the polymer molecular weight, the range of validity of the symmetric parabolic-like behavior given by Eq.(1) shrinks, yielding an asymmetric angle-like coexistence boundary near the theta-point [3] (Fig.1). Physically, it means that in the limit of infinite molecular weight (upon approaching the theta-point) the critical amplitude B_0 and the range of 3D-Ising behavior vanish.

Qualitatively, the phenomenon of separation of a polymer solution into two coexisting phases was explained long ago by Flory [3]. According to the Flory theory, the dependence of the critical temperature T_c and the critical volume fraction ϕ_c of the polymer on the degree of polymerization N is $T_c = \Theta/(1 + 1/\sqrt{N})^2$ and $\phi_c = 1/(1 + \sqrt{N})$, where Θ is the theta-temperature. As elucidated by Widom [4], for any value of the scaling variable $x = \frac{1}{2}\tau\sqrt{N}$ (where N is assumed to be large and τ to be small), the phase coexistence in the Flory system can be represented in terms of a scaling form. The concentration difference $\phi'' - \phi'$, where ϕ'' and ϕ' are the volume fractions of polymer in the concentrated and dilute phases, respectively, is given by

$$\sqrt{N}(\phi'' - \phi') \sim \begin{cases} 2\sqrt{6x} & (x \to 0) \\ 3x & (x \to \infty) \end{cases}. \tag{2}$$
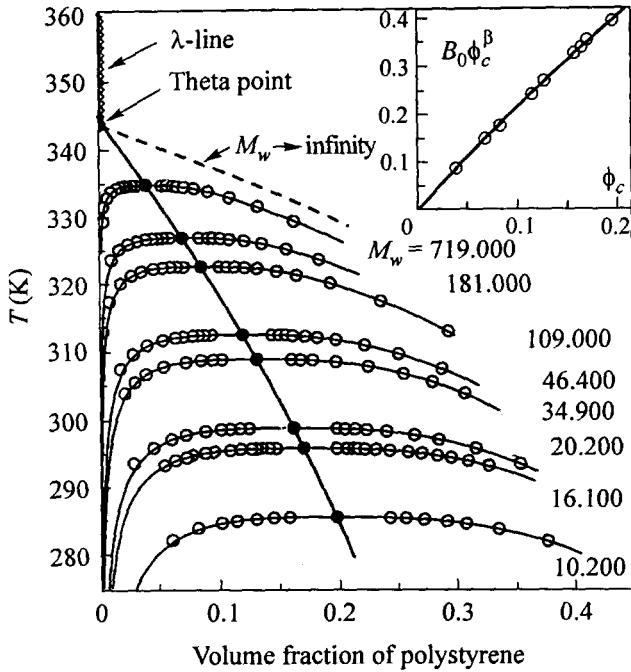
Fig.1. Phase-coexistence curves for solutions of polystyrene of various molecular weights M_w in methyl-cyclohexane. Symbols indicate experimental data by Dobashi et. al. [1]. The insert shows dependence of the critical amplitude B_0 on the critical concentration. Solid curves represent the crossover theory

Although Eq. (2) yields the angle-like coexistence in the theta-point limit ($x \to \infty$), it violates Eq. (1) in the critical-point limit ($x \to 0$). The reason is well known: the Flory theory is essentially a mean-field theory which, just like the van der Waals theory for simple fluids, ignores critical fluctuations. It is possible to modify the Flory model to include critical fluctuations, which does indeed predict both the critical and the theta-point limits correctly as well as the crossover between them [5]. However, restrictions implied by the Flory model for the system-dependent parameters (even after incorporating the fluctuations), and, especially, for the dependence of these parameters upon the degree of polymerization, are too tight to apply the model to real systems.

An attempt to describe the data shown in Fig. 1 by a generalized form of Eq.(2) with $\sqrt{N}$ replaced by ϕ_c^{-1}, the $\sqrt{x}$ by x^β at the limit $x \to 0$, and x by $(T_c - T)/(\Theta - T_c)$ in both limits, was made by Isumi and Miyake [6]. A practical disadvantage of this approach is that, when T_c is close to the theta-temperature (large x), even small changes in Θ (which is not a directly obtainable parameter) cause dramatic changes in x, making the scaling representation extremely sensitive to the choice of Θ.

In this letter we propose a general scaling description of phase separation in polymer solutions. Experiments have shown that ϕ_c does not satisfy the dependence on the degree of polymerization implied by the Flory theory [7]. The description we propose is not based on any specific molecular model and does not incorporate any particular dependence of the critical parameters on the degree of polymerization. Instead, it uses experimentally well defined variables, namely, the reduced temperature distance to the critical point τ and the critical volume fraction ϕ_c. Furthermore, to obtain an explicit form of the scaling function, we have developed a crossover theory by incorporating fluctuations into a Landau expansion near the tricritical point. Furthermore, we shall elucidate the physical nature of the crossover phenomena: very close to the critical phase-separation point the correlation

length of the concentration fluctuations becomes much larger than the polymer molecular size (radius of gyration) and the system exhibits universal 3D Ising behavior. Very close to the theta-point the radius of gyration becomes larger than the correlation length and the system exhibits tricritical mean-field behavior [8].

We assume that a polymer solution can be described by a scaling function $y(z)$ with three universal limits

$$y(z) = \begin{cases} \pm K z^\beta & (z \to 0), \\ \frac{1}{2}z & (z \to \infty, \ \text{polymer} - \text{richphase}), \\ 1 & (z \to \infty, \ \text{solvent} - \text{richphase}), \end{cases} \tag{3}$$

where

$$y = A(\phi - \phi_c)/B_0\phi_c^\beta, \quad z = C\,|\tau|\,/\phi_c, \tag{4}$$

and $K = AC^{-\beta}$ with A and C being system-dependent coefficients. The coefficient C defines the limiting $(M_w \to \infty)$ slope of the phase-separation boundary (Fig.1). The coefficient A can be obtained from a linear correlation between the asymptotic amplitude B_0 and $\phi_c^{1-\beta}$ (insert in Fig.1) for high molecular weights of polymer (small ϕ_c), so that $y = (\phi - \phi_c)/\phi_c$ in this limit. The coefficient A becomes a weak function of ϕ_c for lower molecular weights and thus allows for incorporating non-asymptotic regular effects. The Ising limit in Eq.(3) will be perfectly universal for different systems if the coefficient $K = A/C^\beta$ is not system-dependent. Although there is no theoretical proof for such universality, for the three polymer solutions we have analyzed, the combination $AC^{-\beta}$ turns out to be the same.

In Fig.2 we show coexistence-curve data obtained by Dobashi et al. [1] for polystyrene in methylcyclohexane, by Xia et al. [9] for polymethylmethacrylate in 3-octanone, and by
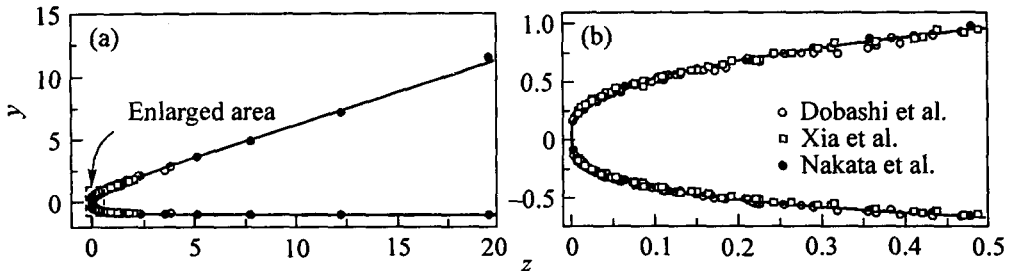

Fig.2. Universal scaled coexistence curve of polymer solutions: (a) the entire range, (b) the critical region. Solid line is calculated from the crossover theory

Nakata et al. [10] for polystyrene in cyclohexane, scaled according to Eq.(3). We see that all data points collapse onto a single master curve. In Fig.3, a crossover from critical Ising behavior (for $z \ll 1$) to the theta behavior (for $z \gg 1$) is clearly seen. As z increases, the volume fraction ϕ' of the solvent-rich phase goes to zero (the "ideal-gas" limit), while the volume fraction ϕ''/ϕ_c of the polymer-rich phase tends to its theta limit $\frac{1}{2}z$, indicated in Fig.3 by the dashed line. The slope of the dashed line on a double logarithmic scale corresponds to the tricritical value of $\beta = 1$.

De Gennes [11] has pointed out that the theta-point in the polymer-solvent system is a tricritical point. A tricritical point is a point which separates lines of second-order
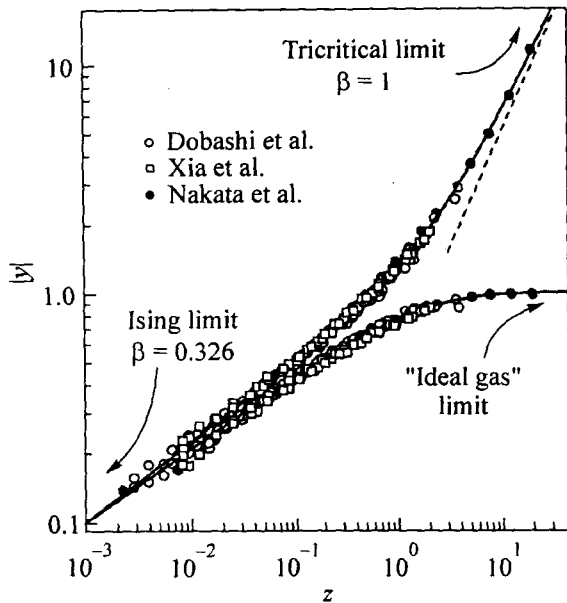
Fig.3. Universal scaled coexistence curve of polymer solution in a double-logarithmic scale showing crossover from Ising behavior to "ideal gas" and tricritical (theta-point) behavior. Solid line is calculated from the crossover theory

(λ-line) and first-order transitions. The states above the theta-temperature on the $\phi = 0$ (shown by the cogged line in Fig.1) correspond to the critical-like self-avoiding-walk singularities associated with the behavior of long ($N \to \infty$) polymer molecules at infinite dilution [11, 12]. This λ-line is associated with an n-component vector order parameter (ψ) in the limit $n \to 0$ [11]. The field h, conjugate to the order parameter, is zero along the λ-line but it becomes non-zero for finite degrees of polymerization. The correlation length associated with the order parameter is the radius of gyration, which diverges in the limit of infinite degree of polymerization (zero field). Below the theta (tricritical) point, the polymer order parameter exhibits a discontinuity accompanied by phase separation and by a discontinuity in the concentration of the polymer. The line of critical phase-separation points shown in Fig.1 is a nonzero-field critical ("wing") line originating from the tricritical point. The order parameter for the fluid-fluid phase separation, associated with the concentration ϕ, and the polymer order parameter ψ belong to different classes of universality. Tricriticality emerges as a result of a coupling between these two order parameters and exhibits mean-field behavior with small logarithmic corrections [13]. Physically, ψ is proportional to the concentration of end points of the polymer chain, while the concentration ϕ is proportional to $|\psi|^2$ [11]. Therefore, a proper description of the phase separation near the tricritical point should incorporate a crossover between Ising critical behavior and (almost) mean-field tricritical behavior.

To obtain an explicit form of the proposed scaling description, we start with the Landau expansion of the critical part of the dimensionless thermodynamic potential $\Delta\tilde{\Omega}$ of a two-component system in the vicinity of the tricritical point in powers of the order parameter ψ [14]:

$$\Delta\tilde{\Omega} = \tilde{\tau}\psi^2 - \lambda\psi^4 + v\psi^6 - h\psi, \qquad (5)$$

where h is the ordering field; $\tilde{\tau} = a(\Delta\tilde{\mu} + b\Delta\tilde{T})$ is the temperature-like scaling field, $\Delta\tilde{T} = (T - \Theta)/T$ with Θ being the tricritical (theta) temperature, $\Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_\Theta$ with

841

$\bar{\mu} = (\mu_2/v_2 - \mu_1/v_1)/RT$ being the reduced polymer/solvent chemical potential difference, v_2 and v_1 the corresponding molecular volumes, $\bar{\mu}_\Theta$ is the value of the chemical potential at the tricritical (theta) point; $\lambda = \lambda_0 \Delta\bar{\mu}$; a, b, λ_0, and v are system-dependent parameters. The conditions $h = 0$ and $\bar{\tau} = 0$ determine the λ-line. At the tricritical point, the coefficient λ changes its sign, being negative along the λ-line above Θ and positive below Θ.

The equilibrium values ψ' and ψ'' of the order parameter are found from the conditions $(\partial\Delta\tilde{\Omega}/\partial\psi)_{T,h} = 0$ and $\Delta\tilde{\Omega}(\psi') = \Delta\tilde{\Omega}(\psi'')$. The concentration (volume fraction) ϕ is related to the polymer order parameter ψ by

$$\phi = \left(\frac{\partial\Delta\tilde{\Omega}}{\partial\Delta\bar{\mu}}\right)_{T,h} = a\psi^2 - \lambda_0\psi^4. \qquad (6)$$

In the limit of infinite degree of polymerization ($h = 0$), we find for the limiting phase-separation boundary shown by the dashed line in Fig.1:

$$\phi' = 0, \qquad \phi'' = \frac{\lambda_0 a}{2v}b|\Delta\tilde{T}|\left[1 - \frac{\lambda_0^2}{4va}b|\Delta\tilde{T}|\right]. \qquad (7)$$

At non-zero h, a phase separation ("wing") critical line emerges, defined by

$$\psi_c^2(h) = \frac{1}{4}\left(\frac{2h}{v}\right)^{2/5} \simeq \phi_c/a, \qquad (8)$$

$$T_c(h) = \Theta\left\{1 + \frac{5v}{\lambda_0 ab}\left[a\psi_c^2(h) - 3\lambda_0\psi_c^4(h)\right]\right\}^{-1}. \qquad (9)$$

Asymptotically, the ratio of the slopes of the limiting ($h = 0$) phase-separation boundary to the critical "wing" line is universal in the Landau expansion and is equal to $5/2$. A comparison between the results obtained from the Landau expansion (5) and from the mean-field Flory model at $N \gg 1$ has shown that the ordering field h can be identified with the degree of polymerization N as $(2h/v)^{-2/5} \sim \sqrt{N}$. Consequently, the near-tricritical Landau model satisfies the mean-field scaling given by Eq. (2).

The Landau theory does not include fluctuations and does not recover the 3D-Ising limit exhibited by real polymer systems. Therefore, we have modified the expansion (5) using the crossover procedure based on the renormalization-group matching method (see [5] and references therein). The details of the calculations will be published elsewhere. The key point of the approach is representing the polymer order parameter as a sum of a regular ψ_0 and a "critical" $\delta\psi$ part $\psi = \psi_0 + \delta\psi$ and rewriting expansion (5) in terms of $\delta\psi$. The critical part is expressed in terms of the distance to the critical temperature (at certain field h) $\tau = [T - T_c(h)]/T$. The crossover procedure is implemented by replacing the temperature variable τ and the order parameter $\delta\psi$ in the corresponding Landau expansion with renormalized quantities $\tau_\times$ and $\delta\psi_\times$, respectively, such that [5]

$$\tau_\times = \tau Y^{-\alpha/2\Delta_s}, \qquad \delta\psi_\times = \delta\psi Y^{(2\gamma-3\nu)/4\Delta_s}, \qquad (10)$$

where α, γ, ν, and Δ_s are universal critical exponents with the following 3D-Ising values adopted in this work: $\alpha = 0.11$, $\gamma = 1.239$, $\nu = 0.630$, and $\Delta_s = 0.51$ [2, 5]. The crossover function Y is to be determined from the equation

$$1 - (1 - \bar{u})Y = \bar{u}[1 + (\Lambda/\kappa)^2]^{1/2}Y^{\nu/\Delta_s}, \qquad (11)$$

where $\bar{u}$, a normalized coupling constant roughly independent of h, and $\Lambda = \Lambda_0 (2h/v)^{2/5}$, a dimensionless "cutoff" wavenumber assumed to be inversely proportional to the radius of gyration R_G, are two crossover parameters. The parameter κ is inversely proportional to the correlation length and serves as an effective distance to the critical point. In the simplest approximation

$$\kappa^2 = -2c_t \tau Y^{(2\nu-1)/\Delta_s}, \tag{12}$$

where the parameter $c_t = c_{t0}(2h/v)^{2/5}$ is associated with the amplitude $\bar{\xi}_0$ of the mean-field correlation length $\bar{\xi}$. Close to the critical point $Y \to (\kappa/\bar{u}\Lambda)^{\Delta_s/\nu} \to 0$ and the thermodynamic properties exhibit 3D-Ising asymptotic behavior. Far away from the critical point, $Y \to 1$, and the mean-field expansion (5) is recovered. The crossover temperature ("Ginzburg number") $\tau_0 \sim (\bar{u}\Lambda)^2/c_t = [(\bar{u}\Lambda_0)^2/c_{t0}](2h/v)^{2/5} \sim \phi_c$ vanishes at the theta (tricritical)-point. The physical origin of the crossover to tricriticality is a competition between the radius of gyration R_G and the correlation length ξ, since $\Lambda/\kappa \sim \xi/R_G$, while the parameter $\Lambda^2/c_t \sim (\bar{\xi}_0/R_G)^2$ defines the crossover temperature τ_0. Specific N-dependencies of the Ising critical amplitudes, predicted by de Gennes' scaling [7, 11], can be also obtained from our theory with the assumption $(2h/v)^{-2/5} \sim \sqrt{N}$.

We have applied the renormalized (crossover) Landau model to describe the experimental data [1, 9, 10] on phase separation in polymer systems and have obtained excellent agreement (solid lines in Figs.1-3). The description of all the systems with a variety of degrees of polymerization requires only four non-universal parameters, namely a, λ_0, $C = \lambda_0 a/v$, and the "bare" crossover temperature $\sim (\bar{u}\Lambda_0)^2/c_{t0}$, which do not depend on molecular weight. Moreover, the combination $(\bar{u}\Lambda_0)^2/c_{t0}$ and $AC^{-\beta}$ can be taken to be the same within the available experimental resolution not only for different molecular-weight samples, but also for different substances. This feature makes the solid curve in Figs.2 and 3 truly universal for all systems studied.

The universality demonstrated in Fig.3 requires both τ and ϕ_c to be small. In first approximation some non-asymptotic effects are incorporated into the universal scaling description. The slight dependence of A on ϕ_c for moderate molecular weights (at larger ϕ_c), shown in Fig.1, absorbs non-asymptotic corrections to the critical limit. A non-asymptotic (at larger τ) non-linearity of the phase separation boundary in the tricritical (zero field) limit can be accounted for by a term quadratic in τ.

Renormalization-group calculations [13] have shown the existence of logarithmic corrections to mean-field tricriticality: the coefficients v and λ_0 in expansion (5) are renormalized, so that the critical line has zero slope at the theta-point. The resolution of the existing experimental data is not sufficient to convincingly determine the logarithmic corrections: the description is equally good with or without the corrections.

---

1. T.Dobashi, M.Nakata, and M.Kaneko, J. Chem. Phys. **72**, 6685 (1980); ibid. **72**, 6692 (1980).
2. J.A.Le Guillou and J.Zinn-Justin, J. Phys. (Paris) **48**, 19 (1987).
3. P.J.Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, 1953, Chap. XIII.
4. B.Widom, Physica **A194**, 532 (1993).
5. A.A.Povodyrev, M.A.Anisimov, and J.V.Sengers, Physica **A264**, 345 (1999).
6. Y.Izumi and Y.Miyake, J. Chem. Phys. **81**, 1501 (1984).

7. I.C.Sanchez, J. Phys. Chem. **93**, 6983 (1989).

8. Yu.B.Melnichenko and G.D.Wignall, Phys. Rev. Lett. **78**, 686 (1997); Y.B.Melnichenko, M.A.Anisimov, A.A.Povodyrev et al., Phys. Rev. Lett. **79**, 5266 (1997).

9. K.Q.Xia, X.-Q.An, and W.G.Shen, J. Chem. Phys. **105**, 6018 (1996); K.Q.Xia, C.Frank, and B.Widom, J. Chem. Phys. **97**, 1446 (1992).

10. M.Nakata, T.Dobashi, N.Kuwahara et al., Phys. Rev. **A18**, 2683 (1978); M.Nakata, N.Kuwahara, and M.Kaneko, J. Chem. Phys. **62**, 4278 (1975).

11. P.G.de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University, Ithaca, 1979.

12. M.E.Fisher, J. Stat. Phys. **75**, 1 (1994).

13. B.Duplantier, J. Phys. (Paris) **43**, 991 (1982).

14. L.D.Landau and E.M.Lifshitz, *Statistical Physics*, Pergamon, New York, 1980.