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Scaling Concepts and the Spinodal and Binodal Curves in Polymer Solutions

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ABSTRACT: After summarizing the Daoud–Jannink scaling theory, which suggests that the binodals in polymer solutions should obey a corresponding-states principle, we show that this result may be approximately derived for both the binodals and spinodals from Flory–Huggins thermodynamics, keeping constant the interaction parameter χ.

This paper is concerned with a corresponding-states property for the spinodals in polymer solutions. This is a family of curves depending on the polymerization number N of the polymer. The binodals are examined subsequently.

Let us first briefly summarize the Daoud–Jannink theory,[1] which, to our knowledge, was the first theory to point out a corresponding-states property for the binodals in polymer solutions, using scaling arguments near a critical point.[2] Following the observation by de Gennes[3] that the Flory Θ temperature should be a tricritical point, Daoud and Jannink elaborated a diagram dividing the concentration–temperature space into four distinct regions, as shown in Figure 1. Regions 1–4 are respectively called the dilute, critical semidilute, tricritical semidilute, and collapsed regions. One may add the biphasic region 5. Included in the dilute range is region 1′, the dilute tricritical or "Θ" region. When one crosses the straight line

$$\tau = (1/\phi^*)\phi \tag{1}$$

where ϕ is the volume fraction of the polymer, $\tau = (T - \Theta)/\Theta$ is the reduced temperature, and ϕ^* is a constant defined below, then, following Daoud and Jannink, a second-order phase transition occurs, which, however, may not be sharp, as a result of a crossover region of finite width. In eq 1, ϕ^* is the volume fraction of the polymer where chains begin to "overlap", or, more precisely

$$\phi^* = N/R_g^3 \tag{2}$$

where R_g^3 is the radius of gyration of the macromolecule. In Θ solvents ϕ^* is proportional to $N^{-1/2}$. If now one crosses the line

$$\tau = -(1/\phi^*)\phi \tag{1′}$$

a first-order transition occurs, and therefore the above authors conclude that this should be an asymptote to the phase equilibrium curves, or binodals (for $\tau N^{1/2} \gg 1$). Since the phase equilibrium curves have two asymptotes, the τ axis and the straight line (1′), Daoud and Jannink guessed that these curves should be hyperbolas. Using scaling arguments, they found that the critical reduced temperature $\tau_c = (T_c - \Theta)/\Theta$ and the critical volume fraction of the polymer ϕ_c should obey

$$\tau_c \sim N^{-1/2} \tag{3}$$

$$\phi_c \sim N^{-1/2} \tag{4}$$

One may notice that relations 3 and 4 follow also from Flory's relations[4,5]

$$\phi_c = \frac{1}{1 + N^{1/2}} \simeq \frac{1}{N^{1/2}} \tag{5}$$

and

$$\frac{1}{T_c} = \frac{1}{\Theta}\left[1 + \frac{1}{\psi}\left(\frac{1}{N^{1/2}} + \frac{1}{2N}\right)\right] \tag{6}$$

where ψ is the entropic parameter, if some evident approximations are made. Knowing the asymptotes and the location of the critical point, Daoud and Jannink wrote the equation of the hyperbola as

$$\frac{\tau N^{1/2}}{-\alpha} = \phi N^{1/2} + \frac{1}{\phi N^{1/2}} \tag{7}$$

where α is some positive constant. This yields a universal curve independent of polymerization number N if one shifts to the new variables $\tau' = \tau N^{1/2}$ and $\phi' = \phi N^{1/2}$.

Daoud and Jannink proceeded by saying that near the critical point the curve should not be a hyperbola, because in this region the polymer system is equivalent to an Ising system and therefore Ising exponents should appear. They, however, assumed a universal form for the binodals as

$$\tau N^{1/2} = f(\phi N^{1/2}) \tag{8}$$

where $f(\phi N^{1/2})$ is some unknown function. On the other hand, Daoud, in his Ph.D. dissertation[6] showed that the spinodals should take such a form and concluded, apparently without further proof, that the same should also hold for the binodals.

We now want to show that equivalent results may be obtained from Flory–Huggins thermodynamics, with the sole assumption that the Flory–Huggins χ parameter is concentration independent.

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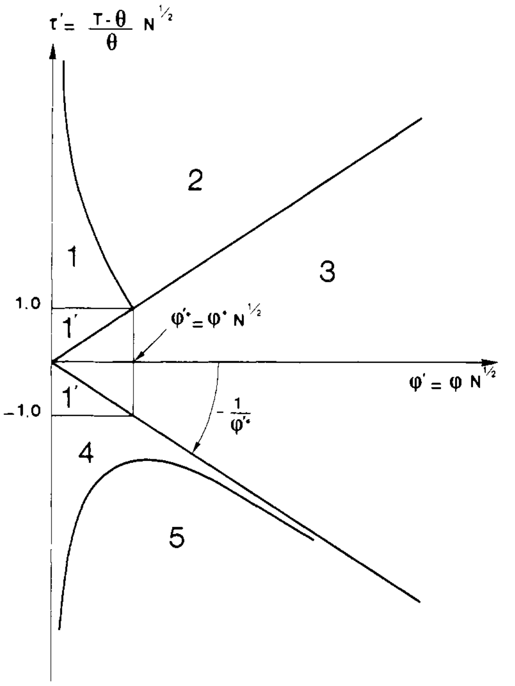

Figure 1. Daoud–Jannink plot in reduced variables near an upper critical solution temperature.[1] $\tau' = [(T - \Theta)/\Theta]N^{1/2}$, where T is the temperature, Θ the Flory temperature, and N the polymerization number of the polymer; $\phi' = \phi N^{1/2}$, where ϕ is the volume fraction (or concentration) of the polymer. Regions 1 (including 1′), 2, 3, 4, and 5 are, respectively, the dilute, critical semidilute, tricritical semidilute, collapsed, and biphasic regions. Different scaling laws hold in regions 1–3 for the radius of gyration, the correlation length, and the osmotic pressure.[1] A symmetric plot should be drawn near a lower critical solution temperature.

Let us consider the Flory–Huggins equation for the excess chemical potential of the solvent:

$$\frac{\Delta\mu_1}{RT} = \ln(1 - \phi) + \left(1 - \frac{1}{N}\right)\phi + \chi\phi^2 \tag{9}$$

where ϕ, usually written ϕ_2, is the volume fraction of the polymer in the solution (no ambiguity arises by eliminating the subscript). The spinodals are the locus of points such as[5]

$$[\mathrm{d}(\Delta\mu_1)/\mathrm{d}\phi] = 0 \tag{10}$$

From eq 9 and 10, χ being considered concentration independent, it is found that the equation of the spinodals is

$$\phi^2 + \phi\left[\frac{1}{2\chi} - \frac{1}{2\chi N} - 1\right] + \frac{1}{2\chi N} = 0 \tag{11}$$

From Flory's theory of phase equilibria,[4] we know that at the critical temperature

$$\chi_c = \frac{(1 + N^{1/2})^2}{2N} \simeq \frac{1}{2} + \frac{1}{N^{1/2}} \tag{12}$$

From eq 6, we find, neglecting higher terms, that

$$\tau_c = \frac{T_c - \Theta}{\Theta} \simeq \frac{1}{\psi N^{1/2}} \tag{13}$$

so that

$$\chi_c \simeq \tfrac{1}{2} - \psi\tau_c \tag{14}$$

or, more generally, since $\partial\chi/\partial\phi = 0$

$$\chi \simeq \tfrac{1}{2} - \psi\tau \tag{14'}$$

Introducing (14′) into (11), we find

$$\phi^2 - \phi\left[\frac{1 - 2\psi\tau N}{(1 - 2\psi\tau)N}\right] + \frac{1}{(1 - 2\psi\tau)N} = 0 \tag{15}$$

At the critical temperature corresponding to the polymerization number N, $|\psi\tau_c|$ is nearly equal to $N^{-1/2}$. When the temperature is lowered below T_c, $\psi\tau$ increases somewhat in absolute value but still remains small with respect to unity for high enough polymerization numbers N. On the other hand, $|\psi\tau N|$ always far exceeds unity, so that (15) may be rewritten with negligible error as

$$\phi^2 + 2\psi\tau\phi + 1/N = 0 \qquad \tau < 0 \tag{15'}$$

This is the equation of a hyperbola whose axes are the axis $\phi = 0$ and the straight line

$$\phi + 2\psi\tau = 0 \tag{16}$$

Equation 15′ takes a form independent of N when the new variables $\phi' = \phi N^{1/2}$ and $\tau' = \tau N^{1/2}$ are introduced:

$$\phi'^2 + 2\psi\tau'\phi' + 1 = 0 \qquad \tau' < 0 \tag{15''}$$

This is the corresponding-states equation for the spinodals. It is equivalent to eq 7 if α is allowed to take the value $(2\psi)^{-1}$.

Allowing for the minor approximations involved in eq 14′ and 15′, it is seen that the Daoud–Jannink assumptions, as far as the spinodals are concerned, seem to have a sound basis in Flory–Huggins thermodynamics: there is an asymptotic limit for increasing concentrations and there is a universal corresponding-states curve.

We now show that the binodals also closely obey a corresponding-states principle in the framework of Flory–Huggins thermodynamics, keeping χ constant with concentration. For this, we consider the two equations defining the equality of the chemical potentials of solvent and polymer in the two phases:[4]

$$\ln\frac{1 - \phi^{\mathrm{II}}}{1 - \phi^{\mathrm{I}}} + (\phi^{\mathrm{II}} - \phi^{\mathrm{I}})\left(1 - \frac{1}{N}\right) + \chi[(\phi^{\mathrm{II}})^2 - (\phi^{\mathrm{I}})^2] = 0 \tag{17a}$$

and

$$\frac{1}{N}\ln\frac{\phi^{\mathrm{II}}}{\phi^{\mathrm{I}}} + (\phi^{\mathrm{II}} - \phi^{\mathrm{I}})\left(1 - \frac{1}{N}\right) - (\phi^{\mathrm{II}} - \phi^{\mathrm{I}})[2 - (\phi^{\mathrm{II}} + \phi^{\mathrm{I}})] = 0 \tag{17b}$$

Here, ϕ^{I} is the volume fraction of the polymer in the more dilute phase and ϕ^{II} that in the more concentrated phase.

Expanding eq 17a to the third order in ϕ^{I} and ϕ^{II}, one obtains

$$[(\phi^{\mathrm{II}})^2 - (\phi^{\mathrm{I}})^2](\chi - \tfrac{1}{2}) - (\phi^{\mathrm{II}} - \phi^{\mathrm{I}})/N - \tfrac{1}{3}[(\phi^{\mathrm{II}})^3 - (\phi^{\mathrm{I}})^3] = 0 \tag{17a'}$$

Let us consider the substitution

$$N' = N/a$$

$$\phi'^{\mathrm{I}} = a^{1/2}\phi^{\mathrm{I}}$$

$$\phi'^{\mathrm{II}} = a^{1/2}\phi^{\mathrm{II}}$$

$$(\chi' - \tfrac{1}{2}) = a^{1/2}(\chi - \tfrac{1}{2}) \tag{I}$$

where a is some positive constant.

One easily sees that eq 17a keeps the same form when primed variables are introduced.

Therefore eq 17a obeys a corresponding-states principle defined by substitution I up to the third order in powers of ϕ.

Table I

γ	$N = 10^4$ $\phi^I \times 10^3$	$N = 625$ $(\phi^I \times 10^3)/4$	% difference	$N = 10^4$ $(\chi - {}^1/_2) \times 10^2$	$N = 625$ $[(\chi - {}^1/_2) \times 10^2]/4$	% difference
1.5	8.0167	7.7769	−2.99	1.00538	1.02041	+1.49
10	2.4230	2.3268	−3.97	1.20533	1.23275	+2.27
100	0.3982	0.3744	−5.98	1.61702	1.67324	+3.47
1000	0.05293	0.04879	−7.82	2.02651	2.11635	+3.77

Equation 17b now is best studied by shifting to the new variables

$$u = (\phi^{II} + \phi^{I})/2 \tag{18a}$$

and

$$v = (\phi^{II} - \phi^{I})/2 \tag{18b}$$

so that

$$\frac{1}{N} \ln \frac{u + v}{u - v} + 2v\left(1 - \frac{1}{N}\right) - 4\chi v(1 - u) = 0 \tag{17b$'$}$$

Since $v < u$, we may expand the logarithm in the above equation in powers of v/u.

Making substitution I, multiplying the obtained equation by $u'/2v'$, replacing N' by $(u_c')^{-2}$, and making a few rearrangements, one finally obtains

$$\frac{u_c'^2}{a} \sum_{n=0}^{n=\infty} \frac{1}{2n + 1}\left(\frac{v'}{u'}\right)^{2n} - \frac{u_c'^2 u'}{a^{3/2}} - \frac{2u'}{a^2}(\chi' - 1/2) + \frac{2u'^2(\chi' - 1/2)}{a^{3/2}} + \frac{u'^2}{a} = 0 \tag{17b$''$}$$

It is easily seen that the first term of the sum in eq 17b″ is of the order of u'^2; as $\chi' - {}^1/_2$ is of the order of u', all terms containing $a^{-3/2}$ are of the third order in u' and may be as a first approximation neglected when N is large enough. Equation 17b obeys therefore a corresponding-states principle through substitution I to the second order in u (or ϕ^I and ϕ^{II}). This is not as good as for eq 17a but allows one to foresee that the binodals should approximately obey a corresponding-states principle.

Numerical computation of the binodals using the Flory procedure[7] substantiates the conclusions drawn from eq 17a′ and 17b″. Table I shows values of ϕ^I for $N = 10^4$, values of $\phi^I/4$ for $N = 625$ ($a = 16$), and the corresponding values of $\chi - {}^1/_2$ for various values of the ratio $\gamma = \phi^{II}/\phi^I$.

The relative error increases in both ϕ and $\chi - {}^1/_2$ as γ increases. One sees, however, that the relative error when N goes from 10000 down to 625, which covers a fairly large part of the polymer range, is less than 6% in ϕ and 3.5% in $\chi - {}^1/_2$ for values of γ up to 100.

Therefore, the corresponding-states principle for the binodals, although not rigorously respected as might be expected from eq 17b, may nevertheless be regarded as a useful approximation.

Assuming now that v is different from zero and small compared to u (i.e., we are in the vicinity of the critical point), eq 17b″ yields the following approximate equation relating u and χ, considering only the first power in v/u in the expansion of the logarithm:

$$2N\chi u^2 + [2N(1/2 - \chi) - 1]u + 1 = 0 \tag{18}$$

or

$$\chi = \frac{u(N - 1) + 1}{2Nu(1 - u)} \tag{18$'$}$$

This is an equation for the "rectilinear" diameter. At the limit of $N \rightarrow \infty$, one obtains

$$u \simeq (\chi - 1/2)/\chi \simeq 2(\chi - 1/2) = -2\psi\tau \tag{19}$$

Equation 19 shows that the initial slope of the "rectilinear" diameter is close to ${}^1/_2$ in a u–χ plot (or $-1/2\psi$ in a u–τ plot). This is different from the value 1 that a cursory examination of the binodals published by Tompa[8] might suggest. Although eq 18 for the "rectilinear" diameter has been obtained for $2v = \phi^{II} - \phi^I$ small compared with $2u = \phi^{II} + \phi^I$, i.e., near the critical points, the binodals computed using the Flory procedure[7] show that the slope is nearly constant over several times the critical concentration. This was not analytically evident and permits one to write rectilinear diameter instead of "rectilinear" diameter in a sensitive way. The slope varies in absolute values between $0.57/\psi$ and $0.63/\psi$ when N varies between 4×10^4 and 6.25×10^2, instead of being equal to $0.50/\psi$ as given by approximate eq 18. The equation of the rectilinear diameter is therefore best described as

$$u + \frac{5}{3}\psi\tau + \frac{2}{3N^{1/2}} = 0 \tag{20}$$

within a quite large molecular range.

For $N \rightarrow \infty$, the initial slope of τ vs. ϕ^{II} is half that of τ vs. u in absolute values.

This gives the initial slope of the limiting curve to the binodals (other than the $\phi = 0$ axis) as $-3/(10\psi)$, corresponding to the straight line

$$\phi^{II} + {}^{10}/_3\psi\tau = 0 \tag{21}$$

A quadratic expression for the binodals equivalent to eq 15′ for the spinodals cannot exist. This is so because it may be easily shown that the only hyperbola having one asymptote, the $\phi = 0$ axis, and going through the critical point with zero slope is the spinodal, eq 15′. Therefore, the binodal cannot be a hyperbola or, more generally, a quadratic. (Alternatively, one may say that this is so because Ising exponents should appear near the critical point and that this cannot be fulfilled by considering quadratics.) However, a quadratic approximation to the binodals may exist by taking asymptotes both different from the $\phi = 0$ axis. Such a quadratic approximation may show in a more striking way than the Flory procedure the corresponding-states principle for the binodals. This, however, lies outside the scope of the present paper.

We may summarize the results obtained thus far as follows: both the binodals and the spinodals closely obey a corresponding-states principle in the framework of Flory–Huggins thermodynamics, in conformity with what is suggested with scaling procedures; furthermore, the spinodals are nearly hyperbolas, whereas the binodals are not quadratics even at the limit of $N \rightarrow \infty$.

Figure 2 shows the full set of lines of interest in a binary polymer–solvent system. For high enough values of ϕ, all the straight lines considered present a downward curvature (not shown on the figure).

When universal coordinates, $\phi N^{1/2}$ and $(\chi - {}^1/_2)N^{1/2}$ are considered, all spinodals and binodals reduce to a single curve, insofar as the corresponding-states principle is obeyed. It was shown above that this was very nearly true for high values of N and rigorous at the limit of N infinite.

The one physically serious criticism that can be raised to the above treatment is that χ, contrary to experience, has been considered to be concentration independent.

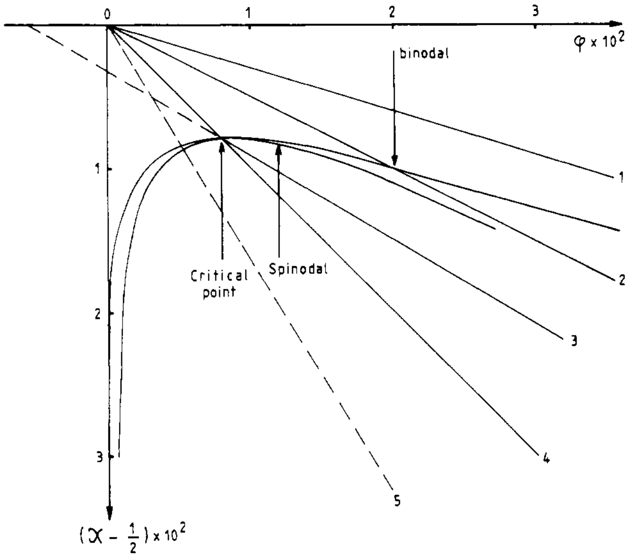

Figure 2. Schematic representation of a binodal, a spinodal, and other lines of interest in ψ and $\chi - {}^1/_2$ coordinates: (1) limiting slope of the envelope to the binodals; (2) asymptote to the spinodals; (3) rectilinear diameter of the binodal; (4) locus of the critical points; (5) axis of the spinodals. One may add the $\phi = 0$ axis, which is an asymptote for both the spinodals and the binodals. The plot in ϕ,τ coordinates is obtained from the above plot through multiplication of the ordinates by ψ^{-1}. The slopes of curves 1, 2, 3, and 4 are, respectively, $-{}^3/_{10}$, $-{}^5/_{10}$, $-{}^6/_{10}$, and -1.

Elaborate work has been done in an attempt to describe the χ variation with concentration from basic principles.[9] These calculations afford, however, only qualitative agreement with experience. Therefore, in any more rigorous calculation on the above lines, $d\chi/d\phi$ values should be taken from experience in specific cases. Neglect of the χ variation with concentration is presumably one reason why the binodals calculated by Flory for the polyisobutylene-diisobutyl ketone system are only in qualitative agreement with experiment.[4]

As a final but important remark, we want to stress the following point: from eq 1′ and 21, it is tempting to make the identification, considering absolute values of ψ

$$ {}^{10}/_3|\psi| \simeq \phi^* \qquad (22)$$

so that the Flory entropy parameter should be essentially related to the flexibility of the polymer chains. Broadly speaking, such an identification is consistent with Flory–Huggins (F–H) thermodynamics but not with Prigogine–Patterson–Flory (P–P–F) thermodynamics.[10-12] Physically, the main difference between F–H and P–P–F thermodynamics is that the latter take account of the motion of the solvent molecules and the polymer segments inside the "cells" defined by their nearest neighbors. From a formal point of view, this leads to a dependence of χ with temperature such that the equation $\chi(T) = \chi_c$ has two solutions, one corresponding to the upper critical solution temperature (UCST) and the other to the lower critical solution temperature (LCST). Thus P–P–F thermodynamics provide the proper physical model permitting an evaluation of the T dependence of χ within the temperature range of the solution. This lies outside the scope of F–H thermodynamics although the form of the free energy of mixing is not affected by the introduction of P–P–F thermodynamics. At the UCST, phase separation occurs mainly for enthalpic reasons, while at the LCST, phase separation occurs mainly for entropic reasons related to the "compression" of the solvent molecules inside "cells" much smaller than that occurring in the free solvent. As this physical fact is not related to chain flexibility, one hardly sees how at the LCST, at least, Flory's entropy parameter could be related to chain flexibility only. It seems therefore that the situation at the UCST and at the LCST regarding the ψ parameter cannot be viewed in a unified way.

Note Added in Proof. After acceptance of the present article it was pointed out to the author that J. F. Joanny (Thèse de Doctorat de 3^e cycle, Université Pierre et Marie Curie Paris VI, 1978) had already studied the spinodals in binary polymer–solvent systems. The equation obtained is somewhat different from eq 15′ as a result of taking an approximate form due to de Gennes for the Flory–Huggins free energy of mixing polymer with solvent.

References and Notes

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