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A note on critical double points of polymer mixtures

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Résumé. — Par un argument général géométrique on prédit le doublement de la valeur de l'exposant β au voisinage d'un point critique double d'une solution ou mélange de polymères. Parce que pour les mélanges la théorie du champ moléculaire du type Flory-Huggins est supposée être applicable, les prédictions sont vérifiées dans le cadre de cette théorie. On étudie en particulier les complications dues à la polydispersité des polymères.

Abstract. — On the basis of a general geometric argument predictions are given for exponent doubling near critical double points of polymer solutions and polymer mixtures. Since for the latter systems mean-field theory of the Flory-Huggins type is supposed to be applicable the predictions are verified within the framework of this theory. Special attention is given to complications arising from the polydisperse character of polymers.

1. Introduction. — Many polymer solutions and some polymer mixtures show a two-phase region at low temperatures, a one-phase region at intermediate temperatures and again a two-phase region at high temperatures (see Fig. 1). The critical points associated with the two misci-

Fig. 1. — Coexistence curves (—) and spinodals (-----) for a binary mixture showing phase separation at high temperatures (above the LCST) and at low temperatures (below the UCST); critical points are indicated by dots, T is the temperature, ϕ the volume fraction of one of the components.

Fig. 2. — Dependence of the location of the miscibility gaps on the degree of polymerization N_1 of component 1 if N_2 and p are kept constant at such values that a critical double point is possible. Curves I : $N_1 < N_{1D}$; there is a UCST ($\times$) and an LCST ($\bullet$). Curves II : $N_1 = N_{1D}$; there is a critical double point ($\blacklozenge$). Curves III : $N_1 > N_{1D}$; no critical state occurs.

bility gaps are called upper and lower critical solution temperatures (UCST and LCST). For strictly binary systems they are situated at the extrema of the coexistence curves or binodals. In figure 1 also the spinodals are indicated. The region between binodal and spinodal is metastable; here phase separation occurs by nucleation. The region confined by a spinodal is unstable; here phase separation occurs spontaneously. The distance between the two-phase regions is strongly influenced by the degrees of polymerization (chain lengths) N_1 and N_2 of the two components and the pressure p . If one increases for instance N_1 and/or N_2 the one-phase region may disappear and the critical temperatures may coincide (Fig. 2, curve II). The point of coincidence is the critical double point. For even larger chain lengths no critical state occurs (Fig. 2, curve III). An example of a polymer mixture for which a critical double point is likely to occur is polystyrene/poly (o-chlorostyrene) [1, 2]. In general it is necessary to have two polymers that are very much alike in order to find both a UCST and an LCST. Otherwise specific interactions are prerequisite for miscibility and only LCST behaviour is possible.

In this note we use a general geometric argument to predict the doubling of the critical exponent β , which is defined by the relation

$$|\varphi_1^A - \varphi_1^B| \sim |T - T_c(N_1, N_2, p)|^\beta \quad (1)$$

where the temperature T is close to the (upper or lower) critical temperature T_c and where φ_1^A and φ_1^B are the volume fractions of component 1 in the two coexisting phases. In practice this result means that in mean-field theory lower and upper coexistence curves are not tangent at the critical double point but form two curves that intersect at the critical double point under a non-zero angle. The validity of the general argument for exponent doubling is explicitly demonstrated for the present case by calculating β from a mean-field theory of the Flory-Huggins type. Such a theory is applicable [3, 4, 5] to describe the critical behaviour of polymer mixtures. In this way we are also able to discuss the complications arising from the polydispersity of the polymers.

2. General argument. — The geometric treatment of critical properties in multi-component systems is based on the work by Griffiths and Wheeler [6]. In the context of critical double points experiment [7] and theory have focussed on gas-gas equilibria of the second kind. The geometric argument [8, 9] for such systems may immediately be transferred to the case of strictly binary polymer mixtures or solutions if we replace the pressure by the temperature and the temperature

by N_1^{-1} , N_2^{-1} or p . We state the predictions from this argument for the case that N_2 and p are fixed; other cases are analogous.

The predictions are the following :

- i) If $N_1 \ll N_{1D}$, β is equal to its « usual value » β_0 ($\beta_0 = 1/2$ in mean-field theories).
- ii) If $N_1 = N_{1D}$, $\beta = 2\beta_0$.
- iii) If N_1 is smaller than and close to N_{1D} , $\beta = \beta_0$ for $|T - T_c| \ll \Delta T_{co}$ and $\beta = 2\beta_0$ for $|T - T_c| \gg \Delta T_{co}(N_1)$ where the « cross-over temperature distance » is defined by

$$\Delta T_{co}(N_1) = 2 |T_c(N_1) - T_c(N_{1D})| \quad (2)$$

with $T_c(N_{1D}) \equiv T_D$ the critical double point temperature. The main assumption entering into the arguments is the analyticity of the inverse function of $T_c(N_1)$. Note that, in contrast to the case of gas-equilibria, here β is defined in the common way as an exponent of the temperature distance to the critical point.

3. Mean-field calculations. — In this section we use a mean-field model to establish the validity of the general predictions for polymer mixtures. This model is a generalized Flory-Huggins model, for which the Gibbs free energy of mixing is given by

$$\Delta G^M/k_B T = (\varphi_1/N_1) \ln \varphi_1 + [(1 - \varphi_1)/N_2] \ln (1 - \varphi_1) + \chi(T) \varphi_1(1 - \varphi_1) \quad (3)$$

where $\chi(T)$ is the Flory-Huggins parameter and where we neglected any pressure dependence for simplicity. Various mean-field theories give explicit expressions for $\chi(T)$. The best-known are the equation-of-state theory [11, 12] and the lattice fluid theory [13]. The equation-of-state theory in particular shows that the additional φ_1 dependence of $\chi(T)$ is only small for the polymer mixtures that we are interested in [1]. For polymer solutions this is usually not the case. We will only consider a φ_1 independent $\chi(T)$. In general $\chi(T)$ will vary with temperature as sketched in figure 3.

De Gennes [4, 5] and Joanny [6] have given arguments why mean-field theory is applicable to mixtures of two components of high degrees of polymerization. In references [5] and [6] this has been done on the basis of equation (3) for $\chi \sim T^{-1}$ or $\chi + \chi_0 \sim T^{-1}$ with χ_0 a constant. If we generalize their arguments to arbitrary $\chi(T)$ we find the following results for the temperature region ΔT^* around T_c where mean-field theory breaks down :

$$\Delta T^*/T_c \sim (N_1 N_2)^{-1/2} |\chi(T_c)/T_c \chi'(T_c)| \quad (4)$$

Fig. 3. — Typical temperature dependence of the Flory-Huggins parameter $\chi(T)$ for systems under consideration. If χ_c is larger than the value χ_D of $\chi(T)$ at the critical double point (◆) there is a UCST, T_1 , and an LCST, T_2 . If $\chi_c < \chi_D$ no critical state occurs.

if $\chi'(T_c) \neq 0$, and

$$\Delta T^*/T_c \sim (N_1 N_2)^{-1/4} |\chi(T_c)/T_c^2 \chi''(T_c)|^{1/2} \quad (5)$$

if $\chi'(T_c) = 0$ and $\chi''(T_c) \neq 0$. The latter situation occurs in the case of exponent doubling (see below). If we assume that the expressions between modulus bars in equations (4) and (5) show negligible chain-length dependence we find that for large N_1 and N_2 the region $\Delta T^*/T_c$ is small. However, for the case of exponent doubling (Eq. 5) the condition of long chains is much stronger⁽¹⁾.

Here we illustrate the exponent doubling by calculating the spinodal, which is given by

$$(\partial^2 \Delta G^M / \partial \phi_1^2)_{p,T} = 0. \quad (6)$$

In the appendix it is shown that the spinodal is described by the same exponent as the coexistence curve. Exponent doubling for the coexistence curve is derived in a similar way by generalizing Joanny's [6] result to arbitrary $\chi(T)$. We prefer the spinodal in order to be able to discuss polydispersity of the components (see section 4).

In the usual way the spinodal volume fractions ϕ_1^+ and ϕ_1^- are derived :

$$\phi_1^\pm = \frac{1}{2}(1 - \tau) \pm \frac{1}{2}[(1 - \tau)^2 - 2(N_1 \chi)^{-1}]^{1/2} \quad (7)$$

where $\tau \equiv (N_1 - N_2)/(2 N_1 N_2 \chi)$. The spinodal volume fractions depend on temperature through the temperature dependence of χ . The critical values of ϕ_1 and χ are well-known :

$$\phi_{1c} = N_2^{1/2}/(N_1^{1/2} + N_2^{1/2}) \quad \text{and} \quad \chi_c = \frac{1}{2}(N_1^{-1/2} + N_2^{-1/2})^2. \quad (8)$$

The critical line in the (N^{-1}, T) plane is given by the implicit relation

$$\chi(T) = \chi_c(N_1) \quad (9)$$

if N_2 is kept fixed. Since $\chi_c(N_1)$ is a monotonously decreasing function of N_1 which adopts all values higher than $\frac{1}{2} N_2^{-1}$, we may use $\chi_c(N_1)$ as a variable equivalent to N_1^{-1} which was used in section 2.

For $\chi(T) > \chi_c(N_1)$ equation (7) will lead to real values of ϕ_1^+ and ϕ_1^- between zero and one ; for $\phi_1^- < \phi < \phi_1^+$ the system will show spontaneous phase separation. If $\chi_c(N_1)$ is larger than the minimum value of $\chi(T)$, equation (9) has two solutions $\chi_c = \chi(T_1) = \chi(T_2)$ with $T_1 < T_2$, where T_1 is a UCST and T_2 is an LCST (see Fig. 3). A critical double point occurs if χ_c coincides with the minimum of the $\chi(T)$ curve.

The exponent β describes how $\phi_1^+ - \phi_1^-$ depends on $T - T_c$. We calculate β by first expanding $(\phi_1^+ - \phi_1^-)^2$ up to lowest order in $\chi - \chi_c$ and by then substituting the expansion of $\chi - \chi_c$ up to lowest order in $T - T_c$ into the result. The first expansion yields to lowest order in $\chi - \chi_c$, that

$$\phi_1^+ - \phi_1^- = 2\sqrt{2}(N_1 N_2)^{3/4} (N_1^{1/2} + N_2^{1/2})^{-2} (\chi - \chi_c)^{1/2} \quad (10)$$

a result which may be checked easily for the special case $N_1 = N_2$. If χ_c is not the extremum of $\chi(T)$ the second expansion yields to lowest order in $T - T_c$, that $\chi(T) - \chi_c \sim |T - T_c|$ so that $\phi_1^+ - \phi_1^- \sim |T - T_c|^{1/2}$ and $\beta = \frac{1}{2}$, which is the usual mean-field value. If χ_c is the extremum of $\chi(T)$ (and thus $d\chi/dT$ vanishes) we have to lowest order in $T - T_c$, that $\chi - \chi_c \sim (T - T_c)^2$ so that $\phi_1^+ - \phi_1^- \sim |T - T_c|$ and $\beta = 1$, which is twice the usual value. In the derivation of these results we assumed that $\chi(T)$ is analytic and $(d^2 \chi / dT^2)_{T=T_D} \neq 0$.

(1) This holds the more, if we use Joanny's criterion $\Delta T^*/(T_c - \theta) < 1$ with θ the Flory θ -temperature.

4. **Polydispersity.** — In the last section we considered a binary system. Polymers, however, have a certain molar mass distribution, so that, strictly speaking, a polymer system is a multi-component system. The borderline of a two-phase region for polydisperse samples is called a cloud point curve because it corresponds to the points of incipient phase separation when a homogeneous mixture is heated or cooled at an infinitesimally slow rate. Note that two cloud point compositions at any given temperature are generally not in equilibrium with one another. Therefore, it is no longer possible to consider the critical exponent as defined in equation (1). However, it will become clear that we may still consider the behaviour of a similar exponent, say β' , associated with the shape of the quasi-binary spinodal near its extremum, which in general does not coincide with the critical point.

The Flory-Huggins theory has been extended to include polydispersity [15, 16]. It shows that the calculation of the cloud point curve is considerably more difficult than the calculation of the spinodal and the critical point. For the simplest case of a concentration and chain length independent $\chi(T)$, the expression for the quasi-binary spinodal is given by :

$$(N_{1w} \phi_1)^{-1} + [N_{2w}(1 - \phi_1)]^{-1} - 2 \chi(T) = 0. \quad (11)$$

Here the weight-averages N_{1w} and N_{2w} occur, which reduce to N_1 and N_2 for monodisperse components. The location of the critical point, which lies somewhere on the spinodal, is determined by

$$N_{1z} N_{1w}^{-2} \phi_1^{-2} - N_{2z} N_{2w}^{-2} (1 - \phi_1)^{-2} = a_1 N_{1w}^{-1} \phi_1^{-2} - a_2 N_{2w}^{-1} (1 - \phi_1)^{-2} = 0 \quad (12)$$

where N_{1z} and N_{2z} are the z-average degrees of polymerization, $a_1 \equiv N_{1z}/N_{1w}$ and $a_2 \equiv N_{2z}/N_{2w}$. The critical points coincide only with the extrema of the spinodals defined by equation (11) if $a_1 = a_2$. For $a_1 \neq a_2$ the critical points are shifted away from the extrema [17]. Consider the situation in which both extrema coincide (Fig. 4). This occurs for the temperature T_D' for which $\chi(T)$ has its minimum, and hence $(d\chi/dT) = 0$. Solving equation (11) for ϕ_1 and substituting the expansion of $\chi(T)$ around T_D' into it results again in $\beta' = 1$. If both spinodals are far apart β' will be equal to $\frac{1}{2}$. Hence, the value of the exponent is doubled if both extrema coincide, irrespective of the molecular weight distributions of the polymers.

5. **Concluding remarks.** — The conclusions in the last section are based on the assumption that the χ -parameter is independent of chain length and concentration. In reality the situation is often more complicated. For a number of systems χ seems to depend on chain length, giving rise

Fig. 4. — Schematic representation of the spinodals of a mixture of two polydisperse polymers. The drawing is for the special situation that the extrema of the spinodals coincide, while the critical points (●) are not at the extrema ($a_1 = a_2$).

to such exotic phenomena as two-peaked cloud point curves and spinodals with three extrema [10]. We expect therefore, that a rather narrow molar mass distribution is needed to observe the predicted doubling of the exponent. Finally, it should be stressed that the pressure may be an important additional parameter in obtaining a situation in which the UCST and LCST are close enough to observe the predicted cross-over behaviour [18].

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Appendix. — We show that the spinodal and the coexistence curve are governed by the same exponent β . The scaling function for the chemical potential is

$$\Delta\mu_{12} \sim \Delta\varphi_1 |\Delta\varphi_1|^{\delta-1} h(x)$$

where $\Delta\mu_{12} \equiv \mu_{12}(\varphi_1, T) - \mu_{12}(\varphi_{1c}, T)$ with $\mu_{12} \equiv \mu_1 - \mu_2$ and where δ is a critical exponent. The scaling function $h(x)$ for which only approximate expressions are known depends only on the variable $x \equiv (T - T_c)/|\varphi_1 - \varphi_{1c}|^{1/\beta}$. The coexistence curve, $\Delta\mu_{12} = 0$, corresponds to a value $x = x_0$ such that $h(x_0) = 0$ whereas equation (6) for the spinodal, $\partial\Delta\mu_{12}/\partial\varphi_1 = 0$, yields

$$\Delta\varphi_1 |\Delta\varphi_1|^{\delta-2} [\delta h(x) - \beta^{-1} x(dh(x)/dx)] = 0$$

which is solved for a certain value $x = x_1$. In both cases x is constant and thus

$$|T - T_c| \sim |\varphi_1 - \varphi_{1c}|^{1/\beta}.$$

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