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Scaling of the Surface Tension of Phase-Separated Polymer Solutions

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The tension of the interface between the equilibrium phases of a phase-separated polymer solution is obtained in the simplest mean-field approximation from the functional equation for the composition profile of the interface. For temperatures T near the critical solution temperature T_c, i.e., for Flory parameter χ near χ_c, and for high degrees of polymerization N, the profile and tension scale with $x = N^{1/2}(\chi - \chi_c)$, just as do the compositions of the coexisting phases in mean-field approximation. The surface tension σ in the asymptotic limit $N \to \infty$, $\chi \to \chi_c$ at fixed x, is found to be given by $a^2\sigma/kT_c \sim (2c'/c)^{1/2} N^{-5/4}\Sigma(x)$, where a is the lattice spacing of an underlying lattice (or, roughly, the length of a monomer), c' and c are the vertical and total coordination numbers of the lattice, and $\Sigma(x)$ is a scaling function, known for all x, with the asymptotic behavior $\Sigma(x) \sim 4\sqrt{2}\, x^{3/2}$ as $x \to 0$ and $\Sigma(x) \sim (6\sqrt{2}/5)\, x^{5/2}$ as $x \to \infty$. The latter implies that σ becomes independent of N as $N \to \infty$ at fixed T near T_c; the former implies that σ becomes proportional to $N^{-1/2}(1 - T/T_c)^{3/2}$ as $T \to T_c$ at fixed $N \gg 1$, as found previously.

KEY WORDS: Scaling; surface tension; interfacial tension; critical solution point; phase separation; polymer solutions.

We ask how the tension σ of the interface between phases of a phase-separated polymer solution depends on the degree of polymerization N and on the temperature T for large N and for T near the critical solution temperature T_c.

It was recently remarked[1] that in the simplest mean-field approximation the volume fraction of polymer ϕ would vary with distance through the interface za according to the functional equation

$$2(c'/c)\,\chi\,\Delta^2\phi(z) = M(\phi) \tag{1}$$

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The a in za is the lattice spacing of an underlying lattice, while z is an integer that indexes the lattice planes in the direction (vertical) perpendicular to the plane of the interface (horizontal); c' and c are, respectively, the vertical and total coordination numbers of the lattice ($c'=1$ and $c=6$ for a simple-cubic lattice); and Δ^2 is the second-difference operator: $\Delta^2\phi(z)=\phi(z+1)-2\phi(z)+\phi(z-1)$. The parameter χ is Flory's[2]

$$\chi=\Theta/2T \tag{2}$$

with Θ the theta temperature (independent of N and T). The function $M(\phi)$ in (1) is given by the Flory theory[2] as

$$M(\phi)=\frac{1}{N}\ln\frac{\phi}{\phi'}-\ln\frac{1-\phi}{1-\phi'}-2\chi(\phi-\phi') \tag{3}$$

with ϕ' the volume fraction of polymer in the more dilute phase. This ϕ' and ϕ'' ($>\phi'$), the value of ϕ in the more concentrated phase, satisfy

$$0=\ln\frac{1-\phi''}{1-\phi'}+\left(1-\frac{1}{N}\right)(\phi''-\phi')+\chi(\phi''^2-\phi'^2) \tag{4}$$

and

$$0=\frac{1}{N}\ln\frac{\phi''}{\phi'}-\ln\frac{1-\phi''}{1-\phi'}-2\chi(\phi''-\phi') \tag{5}$$

Because of (5), ϕ' in (3) may be replaced by ϕ'', and also $M(\phi')=M(\phi'')=0$. The interfacial tension σ will be obtained from (1) and (3)–(5) via the function[1] $h(\phi)$, given in Flory theory[2] by

$$h(\phi)=\frac{1}{N}\phi\ln\frac{\phi}{\phi'}+(1-\phi)\ln\frac{1-\phi}{1-\phi'} + \left(1-\frac{1}{N}\right)(\phi-\phi')-\chi(\phi-\phi')^2 \tag{6}$$

and related to $M(\phi)$ by

$$M(\phi)=dh(\phi)/d\phi \tag{7}$$

Because of (4) and (5), ϕ' in (6) may be replaced by ϕ'', and also $h(\phi')=h(\phi'')=0$.

The critical point is at $\phi=\phi_c$, $\chi=\chi_c$, with ϕ_c, χ_c given by[2]

$$\phi_c=(1+N^{1/2})^{-1}, \qquad \chi_c=\tfrac{1}{2}(1+N^{-1/2})^2 \tag{8}$$

We seek from this mean-field theory a scaling formula[3] for the tension σ, to hold in the asymptotic limit $N \to \infty$, $\chi \to \chi_c$. Corresponding scaling formulas for ϕ' and ϕ'' are known in both theory and experiment.[3-8] The mean-field versions of these are required here. We define a scaling variable x,

$$x = N^{1/2}(\chi - \chi_c) \tag{9}$$

and a scaled form ψ of ϕ,

$$\psi = N^{1/2}\phi \tag{10}$$

and then let $N \to \infty$ and $\chi \to \chi_c$ at fixed x; whereupon (4) and (5), with (8), become

$$0 = -\tfrac{1}{3}(\psi_1^2 + \psi_1\psi_2 + \psi_2^2) - 1 + (1 + x)(\psi_1 + \psi_2) \tag{11}$$

and

$$0 = \ln(\psi_2/\psi_1) + \tfrac{1}{2}(\psi_2^2 - \psi_1^2) - 2(1 + x)(\psi_2 - \psi_1) \tag{12}$$

where $\psi_1 = N^{1/2}\phi'$ and $\psi_2 = N^{1/2}\phi''$. Equations (11) and (12) determine the two branches $\psi_1(x)$ and $\psi_2(x)$ of a scaled coexistence curve, shown in Fig. 1. Alternatively, they determine the inverse function $x(\psi)$. These scaling functions have the asymptotic properties

$$\psi_1(x) \sim 3xe^{-3x^2/2}, \qquad \psi_2(x) \sim 3x \qquad (x \to \infty) \tag{13}$$

$$\psi_1(x) \sim 1 - (6x)^{1/2}, \qquad \psi_2(x) \sim 1 + (6x)^{1/2} \qquad (x \to 0) \tag{14}$$

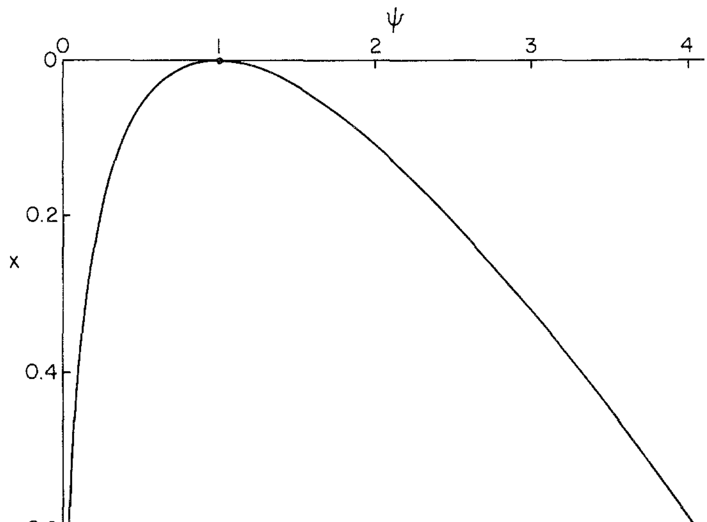

Fig. 1. Scaled coexistence curve, $\psi = N^{1/2}\phi$ versus $x = N^{1/2}(\chi - \chi_c)$. The branch $\psi > 1$ is $\psi_2(x)$, the branch $\psi < 1$ is $\psi_1(x)$. The critical point is at $\psi = 1$, $x = 0$.

Now we apply the same scaling, (9) and (10), to the functional equation for the composition profile, and again let $N \to \infty$ and $\chi \to \chi_c$. Then (1) with (3) becomes

$$(c'/c)\, N^{1/2} \Delta^2 \psi = \ln(\psi/\psi_1) + \tfrac{1}{2}(\psi^2 - \psi_1^2) - 2(1+x)(\psi - \psi_1) \tag{15}$$

By (12), we may replace ψ_1 by ψ_2 on the right-hand side of (15). We also still have $\Delta^2 \psi = 0$ when $\psi = \psi_1$ or ψ_2, just as we had $\Delta^2 \phi = 0$ in (1) when $\phi = \phi'$ or ϕ''. The relevant solution of (15) is such that $\psi \sim \psi_1$ or ψ_2 as $z \to \pm\infty$. The solution ψ is a function of a scaled distance $\zeta = N^{-1/4} z$. Thus, the change in ψ is small when z changes by 1; i.e., in the scaling regime the interface is diffuse; so the second difference $\Delta^2 \psi$ may be replaced by the second derivative $d^2\psi/dz^2$ or by $N^{-1/2}\, d^2\psi/d\zeta^2$. At the same time, in the same scaling regime, the function h in (6) becomes a scaled $H(\psi)$ given by

$$H(\psi) = N^{3/2} h(\phi) \tag{16}$$

$$= \psi \ln(\psi/\psi_1) - \tfrac{1}{3}(\psi^3 - \psi_1^3) + \tfrac{1}{2}\psi(\psi^2 - \psi_1^2) - (\psi - \psi_1) - (1+x)(\psi - \psi_1)^2 \tag{17}$$

Then

$$dH/d\psi = \ln(\psi/\psi_1) + \tfrac{1}{2}(\psi^2 - \psi_1^2) - 2(1+x)(\psi - \psi_1) \tag{18}$$

Because of (11) and (12) we may again replace ψ_1 by ψ_2 on the right-hand sides of (17) and (18), and H and $dH/d\psi$ vanish at $\psi = \psi_1$ and $\psi = \psi_2$. Equation (15) for the profile is now

$$(c'/c)\, d^2\psi/d\zeta^2 = dH/d\psi \tag{19}$$

in scaled form.

The original functional equation (1) for the profile, with (2) and (7), and with the second difference replaced by the corresponding second derivative, is $(c'/c)\, k\Theta\, d^2\phi/dz^2 = kT\, dh(\phi)/d\phi$, with k Boltzmann's constant. From this form of it, we see that the interfacial tension may be obtained as[9]

$$a^2\sigma = (2c'k\Theta/c)^{1/2} \int_{\phi'}^{\phi''} [kTh(\phi)]^{1/2}\, d\phi \tag{20}$$

But in this scaling regime, $T \sim \Theta \sim T_c$. Then, from (10) and (16),

$$a^2\sigma/kT_c = (2c'/c)^{1/2}\, N^{-5/4} \Sigma(x) \tag{21}$$

where $\Sigma(x)$ is the scaling function

$$\Sigma(x)=\int_{\psi_1(x)}^{\psi_2(x)} H(\psi)^{1/2}\,d\psi \tag{22}$$

with $\psi_1(x)$, $\psi_2(x)$, and $H(\psi)$ given by (11), (12), and (17). Equation (21), with (22), is the scaling formula we sought.

The function $\Sigma(x)$ may be obtained numerically from (22), with $\psi_1(x)$ and $\psi_2(x)$ from (11) and (12) (or Fig. 1), and $H(\psi)$ from (17). It is shown in Fig. 2.

The critical behavior is found in the asymptotic limit $x\to 0$. In this limit, from (14), (17), and (22), and with $y=\psi-\psi_1$,

$$\Sigma(x)\sim(12)^{-1/2}\int_0^{2(6x)^{1/2}} y[2(6x)^{1/2}-y]\,dy \qquad (x\to 0) \tag{23}$$

so

$$\Sigma(x)\sim 4\sqrt{2}\,x^{3/2} \qquad (x\to 0) \tag{24}$$

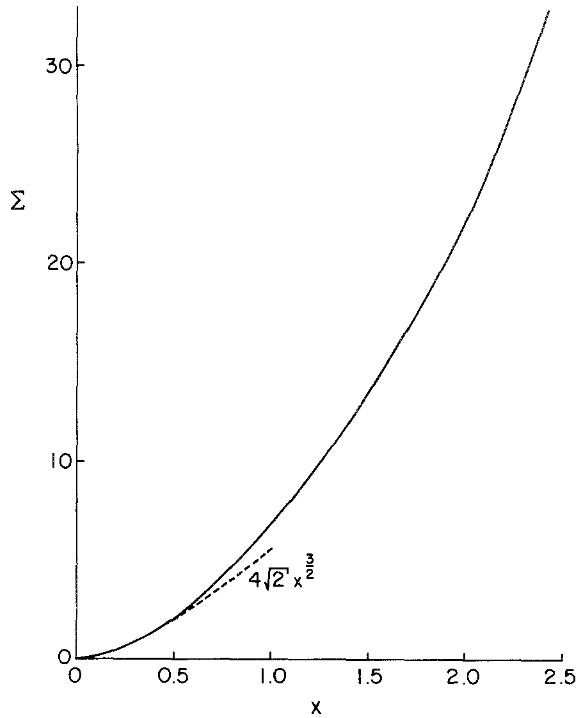

Fig. 2. Scaling function $\Sigma(x)$ for the surface tension (solid curve). The critical point is at the origin. The dashed curve is the $x\to 0$ asymptote: $\Sigma(x)\sim 4\sqrt{2}\,x^{3/2}$.

This asymptote is shown as the dashed curve in Fig. 2. From (2), (9), (21), and (24), the surface tension in this limit is proportional to $N^{-1/2}(T_c - T)^{3/2}$, as already found in this version of the mean-field approximation.[1]

In the other asymptotic limit, $x \to \infty$, we have from (13), (17), and (22),

$$\Sigma(x) \sim 6^{-1/2} \int_0^{3x} \psi^{1/2}(3x - \psi)\, d\psi = (6\sqrt{2}/5)\, x^{5/2} \qquad (x \to \infty) \qquad (25)$$

Then, from (2), (9), and (21) again, the surface tension in this limit is proportional to $(T_c - T)^{5/2}$ and independent of N. That σ would be independent of N in this limit was predictable from (2), (9), (10), and (13), according to which $\phi' \sim 0$ and $\phi'' \sim 3(\chi - \chi_c) \sim \frac{3}{2}(1 - T/T_c)$. Thus, in this limit the dilute phase is essentially pure solvent, while the more concentrated phase has a composition that is independent of N at fixed T. The surface tension, which mainly reflects differences between the two bulk phases, must thus also become independent of N at fixed T in this limit.

The measurements of σ by Shinozaki *et al.*[10] were designed to probe the critical region, $x \to 0$. We see from Fig. 2 that the low-x limit extends up to $x \approx \frac{1}{2}$; there $\Sigma(x) = 2.2$, which is 10% higher than the asymptote $4\sqrt{2}\, x^{3/2} = 2$. The data of Shinozaki *et al.* were indeed taken mostly at $x < \frac{1}{2}$; exceptions were some of the data on their sample of greatest N ($\approx 1 \times 10^4$), which extended to $x \approx 0.9$. At very large N it is hard to probe the critical region $[N^{1/2}(1 - T/T_c) \to 0]$ because of the practical difficulty of making measurements at sufficiently small $1 - T/T_c$.[10]

It would be of interest to extend such measurements to larger x (but still in the scaling regime, $N \gg 1$ and $1 - T/T_c \ll 1$), to obtain a larger part

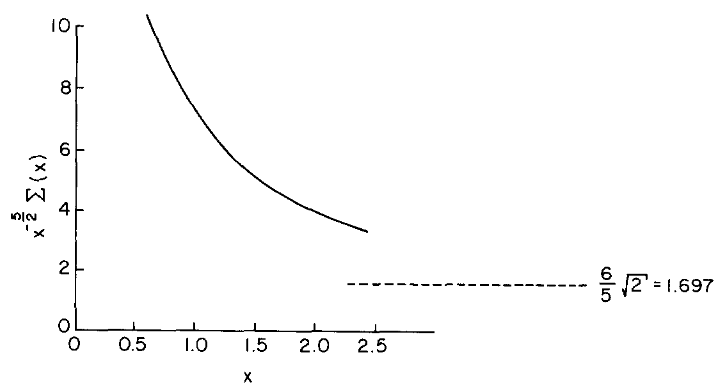

Fig. 3. Plot of $x^{-5/2}\Sigma(x)$ as a function of x, together with its large-x asymptotic limit $6\sqrt{2}/5 = 1.697\ldots$.

of the scaling function $\Sigma(x)$. It will probably not be practical to reach the limit of very large x, where (in mean-field approximation) $\Sigma(x) \sim x^{5/2}$. In Fig. 3 we see that $x^{-5/2}\Sigma(x)$ is still far from its asymptotic limit of $6\sqrt{2}/5 = 1.697...$ even when x is as large as 2.5. Thus, to see behavior corresponding to that in (25) would probably require $x > 10$, say. But to be in the scaling regime at all probably requires $1 - T/T_c < 3 \times 10^{-2}$. Thus, to see the large-x behavior of σ would require $N^{1/2} > 2 \times 10/3 \times 10^{-2}$, or $N > 4 \times 10^5$, which is impractical. But it would be feasible to explore an intermediate range of x and to compare the results, at least qualitatively, with the $\Sigma(x)$ in Fig. 2.

On the theoretical side, it is important to go beyond this version of the mean-field theory to see what effect the corrections have on the scaling of the interfacial tension. Such correction[1,11,12] should change the power of $1 - T/T_c$ in σ in the critical limit ($1 - T/T_c \to 0$ at fixed $N \gg 1$) from 3/2 to 1.26 and the power of N in that limit from $-1/2$ to -0.4; but its effect in the noncritical limit ($N \to \infty$ at fixed $1 - T/T_c \ll 1$) is unknown. Although the present mean-field theory has some obvious defects,[1,13] the surface tension scaling to which it has led may be the prototype of such scaling in more sophisticated theories.

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