Journal of Statistical Physics, Vol. 52, Nos. 5/6, 1988

Note on the Interfacial Tension of Phase-Separated Polymer Solutions

B. Widom[1]

Received March 14, 1988

Earlier theoretical calculations of the interfacial tension σ of phase-separated polymer solutions as a function of the degree of polymerization N and the temperature T, based partly on the mean-field approximation, had led to $\sigma \sim N^{-1/4}(1-T/T_c)^{3/2}$ for fixed $N \gg 1$ and T approaching the critical solution temperature T_c. It is here remarked that the scaling procedure of de Gennes then modifies this to $\sigma \sim N^{-0.37}(1-T/T_c)^{1.26}$, which is in close accord with the experimental $\sigma \sim N^{-0.44}(1-T/T_c)^{1.26}$. The simplest mean-field picture yields $\sigma \sim N^{-1/2}(1-T/T_c)^{3/2}$.

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

I consider a solution of a polymer solute of degree of polymerization N in a solvent, separating into two phases at a temperature T below the critical solution temperature T_c (Fig. 1), and ask how the tension σ of the interface between coexisting phases varies with N and $1-T/T_c$ near the critical point. Nose$^{(1)}$ and Vrij and Roebersen$^{(2)}$ have found in a mean-field approximation

$$\sigma \sim N^{-1/4}(1-T/T_c)^{3/2} \tag{1}$$

Shinozaki *et al.*$^{(3)}$ find by experiment

$$\sigma \sim N^{-0.44 \pm 0.03}(1-T/T_c)^{\mu} \tag{2}$$

with an exponent μ that is essentially the same as the $\mu = 1.26$ expected (and found) at any ordinary critical point,$^{(4)}$ but with the power of N noticeably different from that in Eq. (1).

---

[1] Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853.

0022-4715/88/0900-1343$06.00/0

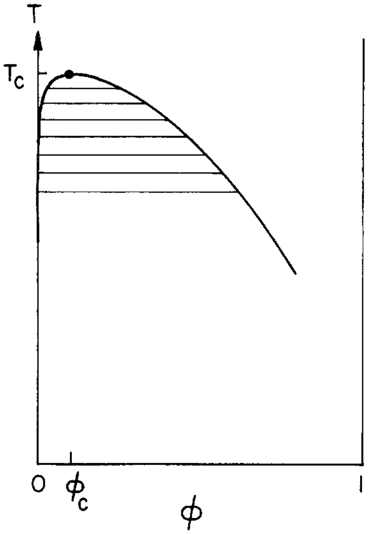

Fig. 1. Temperature (T)–composition (ϕ) coexistence curve for phase equilibrium in solutions of a polymer solute of volume fraction ϕ in a solvent of volume fraction $1-\phi$. The critical solution point is at T_c, ϕ_c, marked with a dot. Some tie lines are shown in the two-phase region.

Shinozaki *et al.*[3,5,6] note that near the critical point the interfacial tension σ should also be related to the correlation length ξ_{corr} of composition fluctuations by[4]

$$\sigma = AkT_c/\xi_{\text{corr}}^2 \tag{3}$$

with some universal[7,8] (in particular, N-independent), dimensionless constant of proportionality A in addition to the Boltzmann constant k. They remark that to within the precision of the measurements of σ, ξ_{corr}, and T_c, Eq. (3) agrees with experiment, with a limiting value of $kT_c/\sigma\xi_{\text{corr}}^2$ at the critical point that is indeed the same, within experimental error, as the apparently universal value for this quantity that is found at the critical points of ordinary, nonpolymeric fluids and liquid mixtures. Moldover *et al.*[9,10] concur. Shinozaki *et al.*[3,5,6] also remark that (3) compares well with (2) if in (3) one uses for the correlation length

$$\xi_{\text{corr}} = aN^{(1-\nu)/2}\,|1-T/T_c|^{-\nu} \tag{4}$$

with a a microscopic length and ν the conventional critical point exponent for divergence of ξ_{corr}; they note that (4) follows from de Gennes' scaling formula (ref. 11; ref. 12, p. 213). Thus, with $\nu = 0.63$, as known from theory and experiment, (3) and (4) imply

$$\sigma \sim N^{-0.37}(1 - T/T_c)^{1.26} \tag{5}$$

in reasonable agreement with (2).

We may now note that a scaling procedure of de Gennes (ref. 12, p. 121) converts (1) directly into (5). We first rewrite (1) as

$$\sigma \sim N^{-1}[N^{1/2}(1 - T/T_c)]^{3/2} \tag{6}$$

and then remark that $N^{1/2}(1 - T/T_c)$ is the scaling variable in the classical (mean-field) theory (ref. 13, p. 509; ref. 12, p. 73). Thus, an immediate correction to the mean-field theory is obtained by altering (6) to

$$\sigma \sim N^{-1}[N^{1/2}(1 - T/T_c)]^{\mu} \tag{7}$$

with μ the correct nonclassical surface tension exponent. This is

$$\sigma \sim N^{-1+\mu/2}(1 - T/T_c)^{\mu} \tag{8}$$

which, with $\mu = 1.26$, is (5). [This is the same argument that yields de Gennes' $N^{-1/2+\beta/2}(1 - T/T_c)^{\beta}$ for the coexistence curve near the critical point (ref. 12, p. 121), starting from the classical $N^{-1/4}(1 - T/T_c)^{1/2}$.]

Another view of (5) or (8) is obtained by noting that there are two alternative routes to the surface tension near a critical point. One may understand$^{(5)}$ the formula (1) as arising from

$$\sigma = h_0 \xi_{\text{interf}} \tag{9}$$

where h_0 is the excess free-energy density in the interface due to its inhomogeneity and ξ_{interf} is the interfacial thickness. In Flory theory the free-energy density (free energy of mixing of polymer and solvent, per unit volume) f, as a function of the volume fraction ϕ of polymer, is given by

$$a^3 f/kT = (1/N)\phi \ln \phi + (1 - \phi)\ln(1 - \phi) + \chi\phi(1 - \phi) \tag{10}$$

where a is again a microscopic length (the cell size in an underlying lattice model, for example) and χ is Flory's interaction parameter

$$\chi = \theta/2T \tag{11}$$

with θ the theta-temperature, a constant (independent of N) characteristic of the polymer and the solvent (ref. 13, pp. 523, 545, 601). The com-

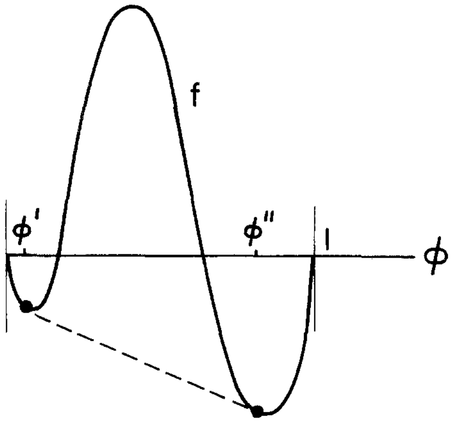

Fig. 2. The common-tangent construction applied to the Flory free energy (10), yielding the polymer volume fractions ϕ' and ϕ'' in the coexisting phases.

positions ϕ' and ϕ'' of coexisting phases are found from (10) by the common-tangent construction, illustrated in Fig. 2. Let us call the height of f above its double-tangent line $h(\phi)$; it is shown in Fig. 3. Near the critical point its maximum value, $h_{\max}$, is such that

$$a^3 h_{\max}/kT_c = (3/4)\,N^{-1/2}(1-T/T_c)^2 \quad (T\to T_c,\ \text{fixed}\ N \gg 1) \tag{12}$$

In mean-field theories of interfacial structure and tension it is found that the nonlocal (i.e., the square-gradient or more general nonlocal-integral) contributions to the free energy of inhomogeneity, and the local contribution from $h(\phi)$, are equal (ref. 4, chaps. 3 and 5). Thus, the h_0 required

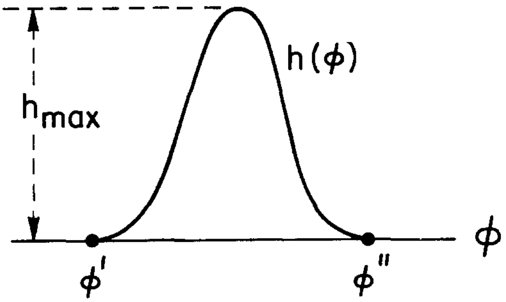

Fig. 3. Height of f above the double-tangent line in Fig. 2 as a function of the polymer volume fraction ϕ.

in (9) may be taken to have the same N and $1-T/T_c$ dependence as $h_{\max}$ in (12):

$$h_0 \simeq h_{\max} \tag{13}$$

with some N-independent proportionality constant. If we also suppose that⁽⁴⁾

$$\xi_{\text{interf}} \simeq \xi_{\text{corr}} \tag{14}$$

with an N-independent proportionality constant, then Eqs. (4), (9), and (12)–(14), with the classical (mean-field) $\nu=\frac{1}{2}$ in (4), yield (1). Although the original derivations⁽¹,²⁾ of (1) were different in form, this was their physical content.

The classical $h_0 \sim N^{-1/2}(1-T/T_c)^2$ from (12) and (13) may now be extended by the same scaling argument that converted (1) into (5). We first rewrite it as $h_0 \sim N^{-3/2}[N^{1/2}(1-T/T_c)]^2$ and then generalize it to $h_0 \sim N^{-3/2}[N^{1/2}(1-T/T_c)]^{2-\alpha}$, where α, in conventional notation, is the index of divergence of a heat capacity. Then (4), (9), and (14), with this generalized, non-classical h_0, yield $\sigma \sim N^{-\frac{1}{2}(\alpha+\nu)}(1-T/T_c)^{2-\alpha-\nu}$. This, by the known scaling law⁽⁴⁾ $\mu+\nu=2-\alpha$, is then (8).

The second route to (5) or (8) is via (3), which more generally is⁽⁴⁾ $\sigma \sim \xi_{\text{corr}}^{-(d-1)}$ in a space of dimensionality d. With (4), this gives $\sigma \sim N^{-\frac{1}{2}(d-1)(1-\nu)}(1-T/T_c)^{(d-1)\nu}$. From the known scaling law⁽⁴⁾ $\mu=(d-1)\nu$ this is $\sigma \sim N^{-\frac{1}{2}(d-1)+\mu/2}(1-T/T_c)^{\mu}$, which, with $d=3$, is again (8).

Note that (8), as just obtained from (3), is found only when $d=3$, whereas when it was obtained by the alternative route via (4), (9), and (14) it was found for any d. That suggests that (4) and (8) may be highly accurate, if not exact, in $d=3$, but not for other d. The same may be said of the scaling arguments by which we have extended the N and $1-T/T_c$ dependences in mean-field formulas into the corresponding nonclassical dependences. The formula (4) may itself be viewed as such an extension of its classical ($\nu=\frac{1}{2}$) version: $\xi_{\text{corr}} \sim N^{1/4}\,|1-T/T_c|^{-1/2}$, which is first rewritten as $\xi_{\text{corr}} \sim N^{1/2}\,|N^{1/2}(1-T/T_c)|^{-1/2}$ and then generalized to $\xi_{\text{corr}} \sim N^{1/2}\,|N^{1/2}(1-T/T_c)|^{-\nu}$.

The theories of Nose⁽¹⁾ and of Vrij and Roebersen,⁽²⁾ while in some respects mean-field theories, go beyond the simplest mean-field theory by allowing the spatial variation of the density of polymer-chain centers to differ from that of the density of monomeric segments. That allows the sizes and shapes of the polymer coils to vary through the interface, which can be important.⁽¹⁾ It is nevertheless of some interest to see what the implications are of the even simpler (though probably less accurate) mean-field theory in which the density of monomeric segments is the only order parameter.

In the Flory theory, Eq. (10), the energetic contribution to the free-energy density f is that of interacting but unconnected segments; that the segments are in reality connected in chains of N segments each is manifested only in the entropic contribution to f, in the factor $1/N$ that multiplies $\phi \ln \phi$. At the same time, in the van der Waals theory of the interfacial composition profile, only the energetic component of the free-energy density is non-local; the entropic component is entirely local (ref. 4, chaps. 3 and 5). Together, these imply that (in this simplest mean-field approximation) the non-local contribution to the free-energy density is independent of N. Then the functional equation for the composition profile $\phi(z)$, with za the distance in the direction perpendicular to the interface, is just (ref. 4, chaps. 3 and 5)

$$2(c'/c)\,\chi \Delta^2\phi(z) = \{\mu[\phi(z)] - \mu_0\}/kT \tag{15}$$

where one imagines an underlying lattice with planes at za, parallel to the interface, for, say, integer z; where c' is the vertical coordination number of the lattice ($c' = 1$ for a simple-cubic lattice) and c the total coordination number ($c = 6$ for simple cubic); where Δ^2 is the second-difference operator, $\Delta^2\phi(z) = \phi(z+1) - 2\phi(z) + \phi(z-1)$; and where

$$\mu(\phi) = a^3\,\partial f(\phi)/\partial\phi, \qquad \mu_0 = \mu(\phi') = \mu(\phi'') \tag{16}$$

The coefficient $2(c'/c)\chi$ of the non-local $\Delta^2\phi$ is independent of N and is just that of a solution of unconnected segments, in agreement with the foregoing discussion; the N-dependence that arises from the chain connectedness is entirely in the local $\mu(\phi) - \mu_0$. This is the essential difference from the earlier, presumably more accurate, treatments.$^{(1,2,14)}$

As $N \to \infty$ for fixed $\chi > \frac{1}{2}$ (thus, for now, not too close to the critical point), the polymer volume fraction ϕ'' in the more concentrated phase, as calculated from (10) and the construction in Fig. 2, is the unique solution $0 < \phi'' < 1$ of

$$0 = \ln(1 - \phi'') + \phi'' + \chi\phi''^2 \tag{17}$$

asymptotically independent of N; while the polymer volume fraction ϕ' in the more dilute phase is exponentially small,

$$\phi' = \phi'' \exp\{-N[(1 - 2/\phi'')\ln(1 - \phi'') - 2]\}. \tag{18}$$

This manifests itself in an extreme asymmetry of the profile. As $\phi(z) \to \phi''$ or ϕ' in the bulk phases ($z \to \pm\infty$), its deviation from its asymptote is exponential in z with decay length

$$a^{-1}\xi_{\text{interf}} = [(c/2c'\chi kT)\,\partial\mu/\partial\phi]^{-1/2} \tag{19}$$

in which $\partial\mu/\partial\phi$ is to be evaluated at $\phi=\phi''$ or at $\phi=\phi'$, respectively. From (10) and (16)–(19) it follows that, at some distance from the critical point, the interface would have a diffuseness of order a on the ϕ'' (more concentrated) side, but would be essentially infinitely sharp [thickness of order $a\exp(-N)$] on the ϕ' (more dilute) side. Such an asymmetry away from the critical point was remarked also by Nose.(1) It is illustrated schematically in Fig. 4.

In the opposite limit, in which $T\to T_c$ at fixed $N\gg 1$, we obtain the characteristic critical behavior. Now $\phi'\to\phi''$ and the profile $\phi(z)$ becomes symmetric: the exponential decay length is still given by (19), but the factor $\partial\mu/\partial\phi$, which is to be evaluated at $\phi=\phi'$ and at $\phi=\phi''$ on the two sides, takes on asymptotically equal values (vanishing as $T\to T_c$). For the characteristic critical behavior to be seen, T must be within some δT of T_c, where in mean-field approximation $\delta T/T_c\approx 1/\sqrt{N}$; i.e., the width in temperature of what we may call the critical region, where ϕ' and ϕ'', say, instead of satisfying (17) and (18), are comparable (both approximately $1/\sqrt{N}$, in mean-field approximation), decreases with increasing N. That means that the determination of the critical behavior of σ by experiment, as in (2), requires that measurements be made at temperatures all the closer to T_c the larger N is. That puts a limit on how large N can be allowed to be in practice, as Shinozaki *et al.*(3) have observed.

We find from (10), (11), (16), and (19) that in this critical regime,

$$\xi_{\text{interf}}\sim a(1-T/T_c)^{-1/2}\qquad (T\to T_c,\ \text{fixed}\ N\gg 1)\tag{20}$$

asymptotically independent of N. This differs from (4) and (14), which,

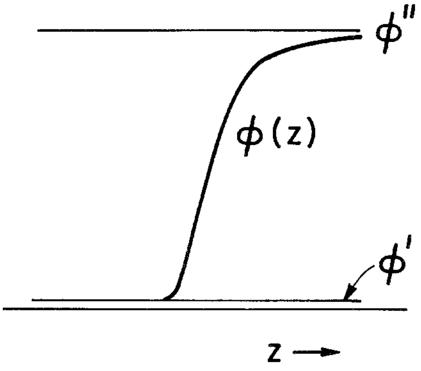

Fig. 4. Interfacial composition profile $\phi(z)$ at some distance from the critical point, showing great asymmetry: in the simplest mean-field theory the interface has a thickness of order a on the ϕ'' (more concentrated) side but is essentially infinitely sharp on the ϕ' (more dilute) side.

with the classical $\nu = \frac{1}{2}$, give $\xi_{\text{interf}} \sim N^{1/4}(1 - T/T_c)^{-1/2}$. Now from (9), (12), (13), and (20),

$$\sigma \sim N^{-1/2}(1 - T/T_c)^{3/2} \tag{21}$$

as the simplest mean-field result, instead of (1).

Equation (21) is a special case of the result previously derived by Sanchez(15) in his treatment of the interfacial properties of polymer blends; it is obtained from his more general formula when one of the polymers of the blend becomes a monomeric solvent. Sanchez also found that the interfacial thickness is independent of N at fixed $1 - T/T_c$, as in (20).

The N dependence in (21) is in better accord with that in the experimental (2) than is that in (1). It does not do as well, however, when extended into a nonclassical formula by the usual scaling argument, first rewriting it as $\sigma \sim N^{-5/4}[N^{1/2}(1 - T/T_c)]^{3/2}$ and then generalizing it to $\sigma \sim N^{-5/4}[N^{1/2}(1 - T/T_c)]^{\mu}$. With $\mu = 1.26$, the resulting power of N is -0.62, to be compared with the experimental -0.44 ± 0.03 in (2) and with the theoretical -0.37 from (8).

This mean-field theory, though, has the advantage of being very simple. It allows one to analyze the dependence of σ on the scaling variable $x = N^{1/2}(1 - T/T_c)$ for all values of x, both large and small, in the scaling regime $N \to \infty$, $1 - T/T_c \to 0$, which could be the prototype of such an analysis in a more sophisticated theory. Such a study of the variation of σ with x through the whole scaling regime in this simplest mean-field theory is the subject of a sequel to this article.(16)

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation and the Cornell University Materials Science Center. The author is grateful to Dr. I. C. Sanchez for helpful correspondence. Dr. Sanchez independently made some of the same points as those in this note.

REFERENCES

1. T. Nose, *Polymer J. (Japan)* **8**:96 (1976).
2. A. Vrij and G. J. Roebersen, *J. Polym. Sci. Polym. Phys. Ed.* **15**:109 (1977).
3. K. Shinozaki, T. van Tan, Y. Saito, and T. Nose, *Polymer* **23**:728 (1982).
4. J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford, 1982), Ch. 9.
5. K. Shinozaki and T. Nose, *Polymer J. (Japan)* **13**:1119 (1981).
6. K. Shinozaki, T. Hamada, and T. Nose, *J. Chem. Phys.* **77**:4734 (1982).
7. D. Stauffer, M. Ferer, and M. Wortis, *Phys. Rev. Lett.* **29**:345 (1972).
8. D. Stauffer, *Phys. Lett. A* **44**:261 (1973).
9. M. R. Moldover, *Phys. Rev. A* **31**:1022 (1985).

10. H. Chaar, M. R. Moldover, and J. W. Schmidt, *J. Chem. Phys.* **85**:418 (1986).
11. P. G. de Gennes, *Phys. Lett. A* **26**:313 (1968).
12. P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, 1979).
13. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, 1953).
14. A. Vrij, *J. Polym. Sci. (A-2)* **6**:1919 (1968).
15. I. C. Sanchez, *Ann. Rev. Mat. Sci.* **13**:387 (1983).
16. B. Widom, *J. Stat. Phys.* (1988), in press.