Interfacial tension of phase-separated polymer solutions: comparison between theory and experiments

Heinrich and Wolf recently measured for various polymer/(poor) solvent systems the interfacial tension between the polymer-rich and polymer-poor phases, together with the polymer composition in both coexisting phases[1,2]. They found that the interfacial tension, σ, was related to the molecular weight of chains M and to the difference $\Delta\varphi$ between polymer volume fractions in both phases by the equation:

$$\sigma = CM^{0.5}\Delta\varphi^{3.85} \tag{1}$$

where C depends only on the chemical nature of the polymer and solvent. Equation (1) has been verified for monodisperse polystyrenes in different solvents (cyclohexane, methylcyclohexane) as well as for polyisobutenes[1]. It has also been verified for polydisperse polystyrenes, with M the weight-average molecular weight of chains[2].

As mentioned by Heinrich and Wolf, the exponent 3.85 is close to the Ising prediction for the dependence of interfacial tension on $\Delta\varphi$. This is in accord with theory, which predicts that the critical properties of polymer solutions undergoing liquid–liquid phase separation are in the same universality class as the three-dimensional Ising model[3]. The purpose of this letter is to demonstrate that theory also accounts for the $M^{0.5}$ dependence of the amplitude, and to propose a more general 'master-curve' than equation (1), which includes no system-dependent constant such as C.

Near the critical demixing temperature T_c the interfacial tension (an energy per surface unit) is related to the system relevant energy and length scales, respectively, kT_c and the correlation length of composition fluctuations ξ, as follows[4]:

$$\sigma = A_\sigma kT_c/\xi^2 \tag{2}$$

where A_σ is a numerical constant and k is Boltzmann's constant. For systems belonging to the three-dimensional Ising universality class ξ diverges when T_c is approached ($\tau = 1 - T/T_c \to 0$) as:

$$\xi = A_\xi \tau^{-\nu} \tag{3}$$

where the exponent $\nu \approx 0.63$. When T_c is approached from the two-phase region $\Delta\varphi$ vanishes as:

$$\Delta\varphi = A_\varphi \tau^\beta \tag{4}$$

where $\beta \approx 0.32_5$ is another Ising exponent. Scaling behaviours (3) and (4) have been observed in polymer solutions by several investigators[5] (for a review see ref. 6). In addition, the system-dependent amplitudes A_ξ and A_φ behave as powers of the number of monomers per chain N ($\approx M$)[6].

Near the critical demixing point, polymer solutions are expected to obey the so-called two-scale-factor universality[7], which states that there are two independent dimensionless ratios between the different physical quantities, just as there are two independent critical exponents. One of these universal ratios is A_σ in equation (2). Chaar *et al.*[8], reviewing the literature, concluded that the available experimental data for fluid systems (including polymer solutions) are consistent with two-scale-factor universality; in particular the median value of the ratio $\sigma\xi^2/kT_c$ near T_c (with ξ measured in the one-phase region and σ at a symmetric distance in the two-phase region) equals approximately 0.39:

$$\sigma = 0.39kT_c/\xi^2 \tag{5}$$

which is close to the result obtained from recent Monte–Carlo simulations[9], i.e. 0.36.

For polymer solutions, equations (3) and (4) may be written in a more universal manner provided τ, $\Delta\varphi$ and the correlation length ξ are scaled appropriately. The proper temperature variable is $x = (T_c - T)/(\theta - T_c)$ rather than $\tau = (T_c - T)/T_c$ (θ is the theta temperature where monomer–monomer interactions vanish)[10–13]. ξ is scaled naturally by the unperturbed polymer radius of gyration R_g (i.e. at temperature θ), and polymer fractions by the critical fraction φ_c:

$$\frac{\Delta\varphi}{\varphi_c} = Bx^\beta \tag{6}$$

and

$$\frac{\xi}{R_g} = \Xi x^{-\nu} \tag{7}$$

Equations (6) and (7) are verified within the mean-field (Flory–Huggins and random-phase) approach, where $x \approx N^{1/2}(1 - T/T_c)$, $\varphi_c \approx N^{-1/2}$, $\beta = \nu = 1/2$, and B and Ξ are numerical constants easy to calculate[12]. The key point of the present analysis is to assume that equations (6) and (7) still hold beyond the mean-field approximation[12]. Des Cloizeaux and Jannink, analysing some recent $\Delta\varphi$ and ξ measurements[13,14] of polystyrenes having various molecular weights in methylcyclohexane, found the data consistent with equations (6) and (7) where $\beta = 0.325$, $\nu = 0.63$, $B \approx 3.7$ and $\Xi \approx 0.44$*. Here, these values are also assumed to be universal, i.e. valid for any polymer/solvent system.

Then, from equations (2), (6) and (7)

$$\sigma = 2.0kT_cR_g^{-2}\left(\frac{T_c - T}{\theta - T_c}\right)^{2\nu} \tag{8}$$

and

$$\sigma = 0.013kT_cR_g^{-2}\left(\frac{\Delta\varphi}{\varphi_c}\right)^{2\nu/\beta} \tag{9}$$

Equations (8) and (9) contain no system-dependent constant and can be used to predict the interfacial tension of phase-separated polymer solutions as a function of the distance (in temperature or composition) to the critical point, provided θ, $R_g(\theta)$ and T_c, φ_c are known. Equations (8) and (9) have been tested for polystyrene/methylcyclohexane and cyclohexane systems using critical data measured[1] and literature values[15] for R_g at $T = \theta$: the calculated values for σ fell within 15% of the measured values in ref. 1.

The scaling behaviour of the critical amplitudes for the interfacial tension dependence on ΔT or $\Delta\varphi$ is deduced from equations (8) and (9) and the molecular weight dependences of R_g, $(\theta - T_c)$ and φ_c. At $T \approx \theta$ polymer chains behave as random walks, hence $R_g \approx M^{1/2}$. Experiments with a variety of polymer/solvent systems have shown[13,16,17] that $(\theta - T_c) \approx M^{-1/2}$ (as predicted by Flory)[18] and $\varphi_c \approx M^{-a}$ with $a \approx 0.38$ (the difference with Flory's $a = 1/2$ can be accounted for with a proper analysis of fluctuations in chain configurations)[19]. Then:

$$\sigma \approx M^{\nu-1}(T_c - T)^{2\nu} = M^{-0.37}(T_c - T)^{1.26} \tag{10}$$

an equation first derived and discussed by Widom[20], and:

$$\sigma \approx M^{2\nu a/\beta - 1}\Delta\varphi^{2\nu/\beta} = M^{0.48}\Delta\varphi^{3.88} \tag{11}$$

which is very close to Heinrich and Wolf's experimental finding, equation (1).

---

*In ref. 12, the constant Ξ is 0.443 not 4.43: des Cloizeaux and Jannink have assumed that the ξ given in ref. 14 is in nm, when it is in Å

0032-3861/94/10/2237–02

ACKNOWLEDGEMENT

The author is grateful to Professors Knobler and Scott (UCLA) for pointing out the error in ref. 12.

D. Broseta
Institut Français du Pétrole,
1&4 Avenue de Bois-Préau, BP 311,
92506 Rueil-Malmaison, France

REFERENCES

1 Heinrich, M. and Wolf, B. A. *Polymer* 1992, **33**, 1926
2 Heinrich, M. and Wolf, B. A. *Macromolecules* 1992, **25**, 3817
3 de Gennes, P. G. *J. Phys. Lett.* 1977, **38**, L441
4 Rowlinson, J. S. and Widom, B. 'Molecular Theory of Capillarity', Oxford University Press, Oxford, 1982, Sect. 9.3
5 Shen, W., Smith, G. R., Knobler, C. M. and Scott, R. L. *J. Phys. Chem.* 1991, **95**, 3376
6 Sanchez, I. C. *J. Phys. Chem.* 1989, **93**, 6983
7 Stauffer, D., Ferer, M. and Wortis, M. *Phys. Rev. Lett.* 1972, **29**, 345
8 Chaar, H., Moldover, M. R. and Schmidt, J. W. *J. Chem. Phys.* 1986, **85**, 418
9 Mon, K. K. *Phys. Rev. Lett.* 1988, **60**, 2749
10 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979
11 Widom, B. *Physica A* 1993, **194**, 532
12 des Cloizeaux, J. and Jannink, G. 'Les Polymères en Solution, Leur Modélisation et leur Structure', les Editions de Physique, les Ulis, 1987, Sect. XVI 4
13 Dobashi, T., Nakata, M. and Kaneko, M. *J. Chem. Phys.* 1980, **72**, 6685
14 Shinozaki, K., Hamada, T. and Nose, T. *J. Chem. Phys.* 1982, **77**, 4735
15 In cyclohexane $R_g(\text{Å})=0.275\ M^{1/2}$ (Cotton, J. P., Nierlich, M., Boué, F., Daoud, M., Farnoux, B., Jannink, G., Duplessix, R. and Picot, C. *J. Chem. Phys.* 1976, **65**, 1101), and in methylcyclohexane $R_g=0.288M^{1/2}$ (ref. 12, p. 763)
16 Xia, K.-Q., Franck, C. and Widom, B. *J. Chem. Phys.* 1992, **97**, 1446
17 Perzinski, R., Delsanti, M. and Adam, M. *J. Physique* 1987, **48**, 115
18 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953, Chs XII and XIII
19 Szleifer, I. *J. Chem. Phys.* 1992, **92**, 6940
20 Widom, B. *J. Stat. Phys.* 1988, **53**, 523