LETTER TO THE EDITOR

Critical properties of a system of two molten polymers

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Abstract. We consider a system of two molten polymers of different lengths N_A and N_B when the interaction is repulsive and leads to a segregation below a critical point T_c. It is known that the critical behaviour is of the 'mean field' type if N_A and N_B are comparable. However if $N_B = 1$ (one of the constituents reduced to a small molecule) it is known that the critical exponents are rather of Ising type. In the present Letter, the cross-over between these two behaviours is studied.

We find a Flory–Huggins behaviour as soon as the small chains are themselves real polymers (i.e. $N_B \gg 1$) independently of the ratio N_A/N_B (>1).

1. Introduction

Demixing in a system of two molten polymers has often been observed (Krause 1972). The phase transition diagrams of such systems show a critical point. The Flory–Huggins theory has been extended for these systems (Flory 1953). It predicts 'mean field' exponents for the osmotic compressibility χ and the correlation length ξ (Daoud 1975) near the critical point.

However it is known that in the vicinity of the critical point, the fluctuations play an important role and the mean field approach often fails.

The purpose of this Letter is to estimate the temperature range ΔT^* in which the mean field approach fails and to compare it with a characteristic temperature $\theta - T_c$ (θ is the Flory temperature, T_c is the critical temperature). De Gennes (1977) has shown that for a system of polymer plus solvent ΔT^* is comparable to $\theta - T_c$: this means that the mean field theory is not valid. On the other hand for two molten polymers with the same polymerisation index ΔT^* is much smaller than $\theta - T_c$ (i.e. the mean field theory works). We want to discuss the cross-over between these limiting behaviours. Thus we consider a mixture of two molten polymers with different polymerisation indices N_A and N_B.

Our approach is based on a Ginzburg criterion and follows the lines of de Gennes (1977). Assuming first that the mean field (Flory–Huggins) calculation is qualitatively correct, we estimate the magnitude of the fluctuations near T_c and then decide whether they are dangerous or not.

2. Determination of the critical region ΔT^*

We consider a system of two polymers A and B whose respective polymerisation indices are N_A and N_B, the concentrations being $\rho_A = \rho$ and $\rho_B = 1 - \rho$.

We calculate $\langle\delta\rho^2\rangle$, the fluctuations of the concentration in one 'correlation volume' of size ξ^3, and compare it with the concentration difference between the two phases along the coexistence curve $(\rho_1 - \rho_2)^2$. When $\langle\delta\rho^2\rangle/(\rho_1 - \rho_2)^2$ is small, the fluctuations are not 'dangerous'. The critical interval is thus determined by the relation

$$\frac{\langle\delta\rho^2\rangle}{(\rho_1 - \rho_2)^2} = 1. \tag{1}$$

For the free energy and critical point (Scott 1949) it is convenient to use a lattice model with N sites and a lattice constant 1. The free energy per site is then:

$$\frac{F}{N} = U\rho_A\rho_B + \frac{kT}{N_A}\rho_A \ln \rho_A + \frac{kT}{N_B}\rho_B \ln \rho_B. \tag{2}$$

We assume that the energy of interaction U is independent of T. This corresponds to the first case of de Gennes (1977).

The coexistence line is determined by equating the chemical potentials $\partial F/\partial\rho$ and the osmotic pressures in the two phases. The critical point is defined by the relations $\partial^2 F/\partial\rho^2 = \partial^3 F/\partial\rho^3 = 0$. We find that $kT_c = 2UN_A/(1 + \alpha^{1/2})^2$, and $\rho_c = 1/(1 + \alpha^{1/2})$ where $\alpha = N_A/N_B$.

Now consider the difference of concentration between the two phases $(\rho_1 - \rho_2)^2$. For a very small difference $|T - T_c|$, if the concentration in one phase is $\rho_1 = \rho_c + \delta\rho$, that of the other phase is $\rho_2 = \rho_c - \delta\rho$, where $\delta\rho$ may be calculated by the relation $\partial F/\partial\rho|_{\rho_c+\delta\rho} = \partial F/\partial\rho|_{\rho_c-\delta\rho}$. The difference of concentration turns out to be:

$$(\rho_1 - \rho_2)^2 = \frac{\Delta T}{T_c}\frac{\alpha^{1/2}}{(1 + \alpha^{1/2})^2}. \tag{3}$$

Next we turn to fluctuations. If g_{AA} is the correlation function ($g_{AA} = \langle\rho_A(0)\rho_A(r)\rangle - \rho_A^2$) and $\tilde{g}_{AA}(q)$ is the Fourier transform of g_{AA}, the mean value of the fluctuations is $\langle\delta\rho^2\rangle = \tilde{g}_{AA}(0)/\xi^3$. Thus we have to know $\tilde{g}_{AA}$. An equivalent approach is based on the response function or susceptibility $\tilde{\chi}_{AA} = -\tilde{g}_{AA}/kT$. We derive the functions through an RPA method following de Gennes (1970). To define a susceptibility, we introduce weak potentials $\delta\phi_A$ acting on A and $\delta\phi_B$ acting on B. Under the influence of these potentials, there is a modification of the mean concentrations ρ_A and ρ_B. If $\tilde{\rho}_A$, $\tilde{\rho}_B$, $\delta\tilde{\phi}_A$ and $\delta\tilde{\phi}_B$ are the Fourier transforms of ρ_A, ρ_B, $\delta\phi_A$ and $\delta\phi_B$ respectively:

$$\delta\tilde{\rho}_A = \tilde{\chi}_{AA}^0\delta\tilde{\phi}_A \qquad \tilde{\rho}_B = \tilde{\chi}_{BB}^0\delta\tilde{\phi}_B.$$

In the first approximation the chains are ideal, i.e. $\tilde{\chi}_{AB}^0 = 0$ and $\tilde{\chi}_{AA}^0 = (\rho_A N_A/kT)f_D(\frac{1}{6}N_A q^2)$ where f_D is the Debye function (Debye 1947) ($f_D(x) = (2/x)\{1 - [(1 - e^{-x})/x]\}$). We can expand it for small q because for T near T_c, ξ is large and only small q are important.

But the modification of the concentrations induces a potential: we must replace $\delta\tilde{\phi}_A$ by $\delta\tilde{\phi}_A + U\delta\tilde{\rho}_B + \delta\tilde{\phi}$ and $\delta\tilde{\phi}_B$ by $\delta\tilde{\phi}_B + U\delta\tilde{\rho}_A + \delta\tilde{\phi}$ where $U\delta\tilde{\rho}_B$ and $U\delta\tilde{\rho}_A$ are interaction terms and $\delta\tilde{\phi}$ is a Lagrangian multiplier ensuring that $\delta\tilde{\rho}_A + \delta\tilde{\rho}_B = 0$ because we always have $\rho_A + \rho_B = 1$ (de Gennes 1970).

By writing $\delta\tilde{\rho}_A = \tilde{\chi}_{AA}\delta\tilde{\phi}_A + \tilde{\chi}_{AB}\delta\phi_B$ and $\delta\tilde{\rho}_B = \tilde{\chi}_{BB}\delta\tilde{\phi}_B + \tilde{\chi}_{BA}\delta\tilde{\phi}_A$ we can derive $\tilde{\chi}_{AA}$ and $\tilde{g}_{AA} = -kT\tilde{\chi}_{AA}$:

$$\tilde{g}_{AA}(q) = \left(q^2 \frac{(1+\alpha^{1/2})^2}{\alpha^{1/2}} + \frac{\Delta T}{T_c} \frac{(1+\alpha^{1/2})^2}{N_A}\right)^{-1}.$$

Hence

$$\tilde{g}_{AA}(0) = \frac{T_c}{\Delta T} \frac{N_A}{(1+\alpha^{1/2})^2} \quad \text{and} \quad \frac{1}{\xi^2} = \frac{\Delta T}{T_c} \frac{\alpha^{1/2}}{N_A}.$$

Thus

$$\langle \delta\rho^2 \rangle = \left(\frac{\Delta T}{T_c}\right)^{1/2} \frac{\alpha^{3/4}}{N_A^{1/2}(1+\alpha^{1/2})^2}. \tag{4}$$

The critical region is then given by (using equations (1), (3) and (4)):

$$\Delta T^*/T_c = \alpha^{1/2}/N_A. \tag{5}$$

3. Discussion

Let us assume now that N_A is large and that N_B is smaller than N_A ($\alpha \gg 1$). Thus the concentration ρ_c is small. We can refer to B as the solvent and A as the solute. The first step is then to define the θ temperature of the system. Following Flory (1953) we can expand F/N for small ρ_A

$$\frac{F}{N} = \frac{kT}{N_A}\rho_A \ln \rho_A + \gamma\rho_A + \tfrac{1}{2}\beta\rho_A^2 \qquad \left(\beta = \frac{kT}{N_B} - 2U\right). \tag{6}$$

We define θ as the temperature at which β vanishes. θ is the temperature at which the sign of β changes, at $T < \theta$ the effective interaction favours segregation and demixing can occur. At $T = \theta$ the coils are essentially ideal and the correlation length is proportional to $N^{1/2}$ (the radius of the coils). To know whether the mean field theory is applicable in most of the range of interest we have to compare ΔT^* with $\theta - T_c$. The theory is acceptable only if $\Delta T^*/(\theta - T_c) \ll 1$, $k\theta = 2UN_A/\alpha$, and $\theta - T_c = \theta\alpha^{1/2}/(1+\alpha^{1/2})^2$ (for large α). Thus

$$\frac{\Delta T^*}{\theta - T_c} = \frac{T_c}{\theta} \frac{(1+\alpha^{1/2})^2}{N_A} \frac{\alpha}{N_A} \approx \frac{\alpha}{N_A} = \frac{1}{N_B}. \tag{7}$$

In conclusion, there are three points. Firstly, when $N_A = N_B = N$, $\Delta T^*/(\theta - T_c) = N^{-1}$ is very small, and the mean field theory is applicable. We recover de Gennes' result (de Gennes 1977).

Secondly, when N_B is much larger than unity (though $N_A \gg N_B$), $\Delta T^*/(\theta - T_c)$ is small, and the mean field theory is applicable. The exponents measured experimentally should be $\xi = (T - T_c)^{-1/2}$ and $\chi = (T - T_c)^{-1}$.

Lastly, in the case where $N_B = 1$, $\Delta T^*/(\theta - T_c) \approx 1$. Here the mean field theory is not correct and we expect Ising exponents.

References

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