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QUALITATIVE FEATURES OF POLYMER DEMIXTION

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Résumé. — Nous considérons trois types de points critiques associés à la ségrégation de chaînes polymériques longues et flexibles :

- 1) un polymère dans un mauvais solvant,
- 2) deux polymères fondus (sans solvant),
- 3) deux polymères dilués dans un bon solvant.

Pour tous ces cas, la théorie usuelle (Flory-Huggins) ou ses extensions, implique dès le départ un comportement de *champ moyen* et des exposants critiques classiques. Nous examinons la validité de cette description en appliquant un critère de Ginsburg. Dans les cas (1) et (3), on conclut que les exposants sont non-classiques. Dans le cas (2), la théorie de champ moyen est qualitativement correcte, sauf dans un très petit intervalle de température ΔT près du point critique [$\Delta T \sim T_c N^{-\varphi}$ où N est l'indice de polymérisation].

Abstract. — We consider three types of critical points associated with the segregation of long, flexible, polymer chains :

- 1) one polymer + poor solvent,
- 2) two molten polymer species without solvent,
- 3) two dilute polymer species in a good solvent.

For all these cases the Flory Huggins theory (or its extensions) would lead to a *classical* (mean field) type of critical behaviour. We analyse the critical singularities more closely using a Ginsburg criterion, and conclude that in cases (1) and (3) the critical exponents are *not classical*. But in case (2), the Flory Huggins theory should apply, except for a minute temperature interval ΔT^* near the critical point T_c [$\Delta T^* \sim T_c N^{-\varphi}$, where N is the polymerization index, and φ is a crossover exponent which we calculate for various situations].

Critical points in 3 dimensions are usually much more complex than predicted by mean field theory [1]. However, some special systems do conform with the mean field picture — the most prominent examples being superconducting metals [2] and superfluid helium 3 [3]; this simplification is related to the magnitude of the correlation length ξ

$$\xi = \xi_0 \left(\frac{T_c}{\Delta T} \right)^{1/2} \quad (\text{mean field}) \quad (1)$$

where ΔT is the distance to the critical point T_c , and ξ_0 is the correlation length far from T_c . Mean field behaviour is found near T_c whenever ξ_0 is large compared to the interparticle distance [4].

It is natural to ask if anything similar happens for critical points involving long polymer chains (with a polymerization index $N \gg 1$). The main practical complication here is due to polydispersity. In the

present note, we ignore polydispersity and consider three typical situations (listed in the abstract) :

1) the case of a *single polymer species dissolved in a poor solvent*, at temperatures T slightly below the Θ point [5], is the most familiar : the mean field free energy F (per cm^3) as a function of concentration c has the form [5, 6] :

$$\frac{F}{T} = \frac{c}{N} \ln(c) + \frac{1}{2} v c^2 + \frac{1}{6} w^2 c^3 + \dots \quad (2)$$

where $w = a^3$ is a monomer volume, and

$$v \sim a^3(T - \Theta)/\Theta$$

is weakly negative in the region of interest. From (2) one derives by standard methods [7] the osmotic pressure and the location of the critical point :

$$-v_c = 2 w N^{-1/2}, \quad c_c = w^{-1} N^{-1/2} \quad (\text{mean field}) \quad (3)$$

and the correlation length ($\xi_0 \cong N^{1/4} a$) to be used in eq. (1) [8]. [Note that this value of ξ_0 leads to $\xi = aN^{1/2}$ when $T = \Theta$ exactly, as it should].

We now apply the Ginsburg criterion [9] to find out whether the mean field description is applicable near the critical point. We choose a point close to critical in the two-phase region, with equilibrium concentrations c_+ and c_- . From eq. (2) we have [5] :

$$c_+ - c_- \cong W^{-1} |\Delta v c_c|^{1/2}, \quad |\Delta v| = v_c - v. \quad (4)$$

We consider the corresponding numbers v_+ and v_- of monomers contained in a certain volume Ω . We compare $v_+ - v_- = \Omega(c_+ - c_-)$ to the fluctuations δv in the total number. We know that [10]

$$\delta v^2 = cT \frac{\partial c}{\partial \pi} \Omega \cong |\Delta v|^{-1} \Omega. \quad (5)$$

The importance of the fluctuations is measured by

$$X = [\delta v / (v_+ - v_-)]^2$$

X is maximal when Ω takes the smallest allowed value [9], namely $\Omega = \xi^3$ (or more generally $\Omega = \xi^d$ if we work in d dimensions). Then we find

$$X \cong \left(\frac{\Theta}{\Delta T} \right)^{2-d/2} N^{1/2-d/4}. \quad (6)$$

For $d = 3$ this reduces $X \sim [(\Theta - T_c)/\Delta T]^{1/2}$: thus X is larger than unity throughout the temperature interval $\Delta T \sim \Theta - T_c \sim \Theta N^{-1/2}$ which is of interest for critical phenomena [5] : this means that the fluctuations are *dangerous*, and that the critical behaviour is *not* of the mean field type [9].

2) We turn now to a *molten polymer blend* (A + B) and consider for simplicity a symmetric situation ($N_A = N_B = N$). It is convenient here to use a lattice model, the fractions of A and B per site being ρ and $(1 - \rho)$, and the effective interaction being

$$U = U_{AB} - 1/2(U_{AA} + U_{BB}).$$

The *mean field* free energy per site F_s has the classical mixing form :

$$F_s = U\rho(1 - \rho) + \frac{T}{N} [\rho \ln \rho + (1 - \rho) \ln (1 - \rho)]. \quad (7)$$

Two cases appear to be of interest here :

(i) U small, positive, and essentially temperature independent : this may occur in mixtures of deuterated and nondeuterated polymers of the same structure ⁽¹⁾ ;

(ii) for chemically different species U may be large and of either sign. To reach a critical point at a not too high temperature, we then need to have U depen-

dent on T , and vanishing at one particular temperature T_0 : such a compensation point may indeed occur if A and B have very different thermal expansions. In this case, near $T = T_0$ we may set

$$U = U'(T_0 - T)$$

where U' is a constant of arbitrary sign (and of order unity).

From eq. (7) we derive the location of the critical point

$$U(T_c) = \frac{2 T_c}{N}$$

$$\rho_c = 1/2$$

and the correlation length ξ above T_c (eq. 1) with a prefactor

$$\xi_0 \cong N^{1/2} a \quad (\text{case (i)})$$

$$\xi_0 \cong a \quad (\text{case (ii)}) .$$

The result for case (ii) is surprising at first sight. Note however that when $T = T_0$ (at the compensation point) $\Delta T \sim T_0/N$ and $\xi = \xi_0(T_c/\Delta T)^{1/2}$ is of order $N^{1/2} a$, as it should for a system of molten chains without segregation effects.

We then proceed to construct the Ginsburg argument (in a volume $\Omega = \xi^d$) and find, for instance in case (ii) :

$$(v_+ - v_-)^2 \cong \Omega^2 N \Delta T / T_0$$

$$\delta v^2 \cong \Omega \Delta T / T_0$$

$$X = \frac{\delta v^2}{(v_+ - v_-)^2} = N^{-1} \left(\frac{T_0}{\Delta T} \right)^{2-d/2} \quad (\text{case (ii)}) . \quad (8)$$

In particular, for $d = 3$, X is larger than unity only in a very small temperature interval

$$\Delta T^* \cong T_0 N^{-2} \cong |T_0 - T_c| N^{-1} \ll |T_0 - T_c| .$$

For case (i) a similar argument leads to

$$X = N^{1-d/2} \left(\frac{T_c}{\Delta T} \right)^{2-d/2} \quad (\text{case (i)}) \quad (9)$$

and for $d = 3$ the width of the non classical region is

$$\Delta T^* \sim T_c N^{-1} . \quad (10)$$

Thus for both cases we may say that the existence of long chains reduces the critical region very strongly.

The condition $|\Delta T| > \Delta T^*$ will be realized in most experiments as soon as N is reasonably large : then the fluctuations are not dangerous, and the mean field picture is qualitatively correct.

3) The case of *two (dilute) polymers dissolved in a good solvent* is less familiar [11a]. One example (polystyrene + polyisobutylene + toluene) has recently been studied by light scattering and analysed in mean field [11b]. We may summarize the situation as follows (again assuming symmetry between the

⁽¹⁾ I am indebted to Prof. Buckingham for an explanation of this effect.

two polymers A and B) : the mean field free energy (per cm^3) is :

$$\frac{F}{T} = \frac{1}{2} v_{AA} c_A^2 + v_{AB} c_A c_B + \frac{1}{2} v_{BB} c_B^2 + \frac{T}{N} (c_A \ln c_A + c_B \ln c_B) \quad (11)$$

where all three coefficients v are positive and large (good solvent) but v_{AB} is larger than $v_s = v_{AA} = v_{BB}$:

a) At low concentration c we have separate, swollen coils of radius $R_F = aN^{3/5}$ [5]. In this regime, different coils avoid each other completely, and no segregation can take place.

b) At a concentration $c^* = N/R_F^3 \sim N^{-4/5} a^{-3}$ the coils begin to interpenetrate and the difference between v_{AB} and v_s is felt.

c) At a concentration of may be $2c^*$ (or $3c^*$) the effective interaction between two neighbouring coils J becomes comparable to T , and segregation takes place. This statement may be understood from the scaling laws for single polymer solutions in good solvents [12] : for c larger than c^* the probability of contact between one given monomer and the others is not proportional

to c (as in the mean field theory) but to $c(ca^3)^{1/4}$, the last factor expressing the effect of correlations [12]. Then the effective coupling between two neighbouring chains is of order

$$J(c^*) \sim TNc^*(c^* a^3)^{1/4} (v_{AB} - v_s). \quad (12)$$

Inserting the above formula for c^* and $v_{AB} - v_s \sim a^3$ we are led to $J(c^*) \sim T$.

The analysis shows that the mean field picture is not very adequate for this case, since it does not even locate the critical concentration correctly (c_c is of order N^{-1} in mean field while it is of order $N^{-4/5}$ in reality). What is needed here first is an improved mean field theory, where the effective couplings depend on concentration ($J(c)$). But as regards critical exponents, the situation is clear : just as in case (1) the interaction range is large, but the average distance between coils remains comparable to the interaction range : no special simplification is expected, and the critical exponents should be non-classical.

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