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Demixing of a molten polymer blend in a confined geometry

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Résumé. — On discute ici la ségrégation d'un mélange de polymères fondus monodisperses confinés dans un tube de diamètre D . On trouve que pour $D \gg aN^{1/4}$ (N = nombre de monomères par molécule) la valeur critique du paramètre de Flory χ n'est pas perturbée (i.e. $\chi_c \sim 1/N$). Par contre, pour $D \ll aN^{1/4}$, χ_c croît ($\chi_c \sim (a/D)^4$), augmentant ainsi la miscibilité du mélange. On montre ensuite que dans le cas d'un mélange confiné dans un plan (monocouche), χ_c est donné par l'expression habituelle $\chi_c \sim 1/N$.

Abstract. — We discuss the segregation of a molten monodisperse polymer blend confined in a tube of diameter D . We find that for $D \gg aN^{1/4}$ (N being the number of monomer per chain), the critical value of the Flory parameter χ is unperturbed ($\chi_c \sim 1/N$). For $D \ll aN^{1/4}$, χ_c grows ($\chi_c \sim (a/D)^4$), increasing the blend miscibility. We then show that in the case of a blend confined to a plane (monolayer), χ_c is given by the usual expression $\chi_c \sim 1/N$.

1. Introduction.

In recent years a considerable amount of work has been devoted to the study of binary polymer mixtures [1]-[11]. A standard approach to describe the thermodynamic properties of these systems is the Flory-Huggins lattice model [12]: the chains are inscribed on a cubic lattice of edge a . All sites are filled either by a monomer A (probability φ) or by a monomer B (probability $1 - \varphi$). The free energy per site is then:

$$\frac{F}{kT} = \frac{\varphi}{N_A} \text{Log } \varphi + \frac{1 - \varphi}{N_B} \text{Log } (1 - \varphi) + \chi \varphi (1 - \varphi) \quad (1)$$

(where N_A and N_B are the degrees of polymerization of A and B respectively, T the temperature, and k the Boltzmann constant). In most cases the Flory parameter χ is positive [1] and favors segregation. The critical point of demixing is expected to be well described [1] by the mean field form (1) [3]. In particular, for the symmetric case ($N_A = N_B = N$), the critical value of χ is given by

$$\chi_c = 2/N. \quad (2)$$

For $\chi < \chi_c$, the system is entirely miscible, while for $\chi > \chi_c$ the system may separate into two phases (for a certain range of relative concentration, φ).

Our aim here is to understand how the critical value χ_c of the Flory parameter (Eq. (2)) is modified when the blend is confined in a cylindrical tube of diameter D . (For simplicity we restrict ourselves to the symmetric case.) Our analysis is based on reference [13] where the conformation of molten polymers in small pores is studied [14]. It is restricted to scaling laws : the exact prefactors in all our formulas remain unknown.

2. Molten polymer in a tube.

Let us briefly recall the main results obtained in reference [13]. We consider a melt of polymer chains confined in a tube of diameter D and assume that the wall is repulsive (i.e. no adsorption). When D is large, we are dealing with a three-dimensional system : the chains are ideal, with size $R_0 = N^{1/2} a$. For $D < R_0$, each chain is confined in two directions and spans a certain length R_{\parallel} in the third direction (parallel to the tube axis). The conformation of a chain is controlled by the following two parameters :

— *the internal filling fraction* Φ_{int} corresponding to N monomers spread in a volume $\sim D^2 R_{\parallel}$:

$$\Phi_{\text{int}} \approx Na^3 / (D^2 R_{\parallel}) \quad (3)$$

— *the perturbation parameter* ξ which tells us when the interactions inside one chain become important (for $\xi < 1$ the chain is ideal while for $\xi > 1$ the chain is swollen). It can be shown that in the present case :

$$\xi \approx \Phi_{\text{int}} . \quad (4)$$

Let us first assume that the chain remains ideal (i.e. $R_{\parallel} = R_0$) : Φ_{int} and ξ are then given by

$$\Phi_{\text{int}} \approx \xi \approx N^{1/2} (a/D)^2 . \quad (5)$$

For $D > a \cdot N^{1/4}$, Φ_{int} and ξ are indeed small (see Eq. (5)), as required by the assumption $R_{\parallel} = R_0$. But for $D < a \cdot N^{1/4}$ we cannot have $R_{\parallel} = R_0$ any more since this would lead to values $\Phi_{\text{int}} > 1$. In this regime ($D < N^{1/4} a$), the internal filling fraction takes its maximum allowed value ($\Phi_{\text{int}} = 1$) and R_{\parallel} is given by (see Eq. (3))

$$R_{\parallel} \approx Na^3 D^{-2} ; \quad (6)$$

the chains are spatially segregated, each chain occupying a given length R_{\parallel} of the tube (Eq. (6)).

3. Segregation in a tube.

We now consider the case of an A + B molten polymer blend confined in a tube of diameter D . We take the wall to be repulsive and assume that the interaction between a monomer and the wall is the same for the two polymer species. In the regime $1 < \frac{D}{a} \ll N^{1/4}$, as was shown in section 2, the chains lie in sequence one after the other. Two adjacent chains A and B overlap only in a small region of thickness L (Fig. 1). The free energy of mixing (per lattice site) is now given by

$$\frac{F}{kT} = \frac{\varphi}{N} \text{Log } \varphi + \frac{1-\varphi}{N} \text{Log } (1-\varphi) + \frac{2}{N} \varphi(1-\varphi) \frac{\varepsilon_{AB}}{kT} \quad (7)$$

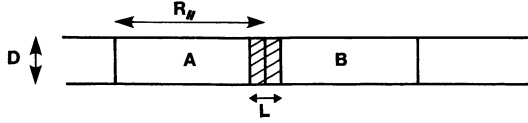


Fig. 1. — A + B polymer blend confined in a tube of diameter D in the regime $1 \leq D/a \ll N^{1/4}$. Each chain occupies a given length R_l of the tube and the chains lie in sequence one after the other. Two adjacent chains A and B overlap in a region of thickness L (shaded area).

where ϵ_{AB} represents the energy associated to the boundary between an A-chain and a B-chain. The volume of the interfacial region is given by $\sim LD^2$ and we can write roughly :

$$\epsilon_{AB} \sim LD^2 \frac{kT\chi}{a^3}. \tag{8}$$

For $\frac{1}{N} \ll \chi \ll 1$, the characteristic thickness of the interface has been previously [15] predicted to vary as $a \cdot \chi^{-1/2}$ in three dimensions, a result which is in reasonable agreement with experiments [16]. Let us first assume that this interfacial thickness is not modified by the confinement, i.e. :

$$L \sim a\chi^{-1/2} \tag{9}$$

(we shall see that this assumption is indeed valid in a certain range of diameters D). This leads to

$$\frac{1}{kT} \epsilon_{AB} \sim \chi^{1/2} (D/a)^2. \tag{10}$$

Since we are now dealing with a one dimensional system and short range couplings we cannot strictly define a critical point and a critical value of ϵ_{AB} . However, a standard analysis *via* transfer matrices [17] shows that there is at least a crossoverpoint between an uncorrelated mixtures and a situation with long correlated « trains » of identical chains. The crossover point corresponds to $\epsilon_{AB} \sim kT$. The corresponding value of χ (which we shall still call χ_c) is

$$\chi_c \sim (D/a)^{-4}. \tag{11}$$

For $D = aN^{1/4}$, we recover the three-dimensional value $\chi_c \sim 1/N$. With the assumption $L \sim a \cdot \chi^{-1/2}$, the variation of χ_c with D is thus given by (see Fig. 2) :

$$\chi_c \sim \frac{1}{N} \quad \text{for} \left(\frac{D}{a} \right) \gg N^{1/4} \tag{12}$$

and

$$\chi_c \sim \left(\frac{a}{D} \right)^4 \quad \text{for} 1 \leq \left(\frac{D}{a} \right) \ll N^{1/4}.$$

However, the approximation $L \sim a \cdot \chi^{-1/2}$ cannot be valid for all values of D : for $D = a$, equation (10) leads to $\frac{\epsilon_{AB}}{kT} \sim \chi^{1/2}$ while in one dimension the interfacial energy must be proportional to χ ($\epsilon_{AB}/kT \sim \chi$ for $D = a$). In order to determine the critical value of D below which expression (10) ceases to be valid, it is useful to recall a qualitative derivation for the three-dimensional interfacial thickness [18]. Let us consider a sharp A-B boundary

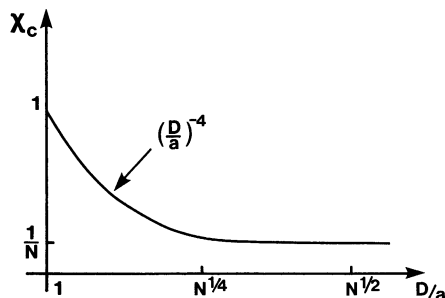


Fig. 2. — Variation of the critical value of the Flory parameter χ_c with the diameter D of the tube.

(Fig. 3). We expect a portion of the A-chain (n monomers) to enter the B-phase if $n\chi \leq 1$. Such a portion of the chain extends over a distance $\sim a \cdot n^{1/2}$ and one indeed recovers the expression $a \cdot \chi^{-1/2}$. The above argument explicitly assumes that (i) the portion of n monomers of the A-chain is completely surrounded by B-monomers, (ii) this portion extends over a distance $\sim a \cdot n^{1/2}$. However, we know from reference [13] that the above two assumptions cease to be valid for an n -monomers chain confined in a tube whose diameter is smaller than $a \cdot n^{1/4}$. Consequently, the expression (10) is not valid for $D < a\chi^{-1/4}$. In this case, we can look for the following scaling form for ε_{AB} :

$$\frac{1}{kT} \varepsilon_{AB} \sim \chi \left(\frac{D}{a} \right)^\beta. \quad (13)$$

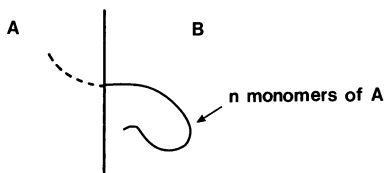


Fig. 3. — An interface between A and B polymers. A portion of an A-chain (n monomers) may enter the B phase if $n \cdot \chi \leq 1$. Such a portion of the chain extends over a distance $\sim a \cdot \chi^{-1/2}$ and the overall thickness of the interface is given by $\sim a \cdot \chi^{-1/2}$.

The continuity of ε_{AB} at $D = a\chi^{-1/4}$ implies that $\beta = 4$. We then have :

$$\frac{\varepsilon_{AB}}{kT} \sim \chi^{1/2} (D/a)^2 \quad \text{for } (D/a) > \chi^{-1/4}$$

and

$$\frac{\varepsilon_{AB}}{kT} \sim \chi (D/a)^4 \quad \text{for } (D/a) < \chi^{-1/4}.$$

From equations (14) the critical value of χ is :

$$\chi_c \sim \left(\frac{a}{D} \right)^4 \quad \left(1 \leq \frac{D}{a} \ll N^{1/4} \right). \quad (15)$$

Note that using the preceding procedure, we recover equation (11).

4. Discussion.

It is important to notice that the chains may have difficulty re-arranging themselves (A. Silberberg, private communication) : to pass through a B-chain, an A-chain must get over a potential barrier which becomes large with regard to kT for $D \ll aN^{1/4}$. In that case, equilibration times might thus become very long.

Let us briefly consider the case of a molten polymer blend confined to a plane (monolayer). Even for $\chi = 0$ the chains are segregated [19], each chain occupying a surface $\sim N \cdot a^2$. The interfacial energy ε_{AB} can be estimated by cutting out the plane in hexagons, each containing a single chain (Fig. 4). Two adjacent chains A and B overlap in a region of surface $\sim aN^{1/2}L$ (where L is the interface thickness). We can write :

$$\varepsilon_{AB} \sim (a \cdot N^{1/2}) L \frac{kT\chi}{a^2} \sim N^{1/2}\chi^{1/2}. \quad (16)$$

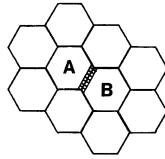


Fig. 4. — Schematic representation of a molten polymer blend A + B confined to a plane (monolayer). Each hexagon (surface $\sim N \cdot a^2$) is occupied by a single chain. Two adjacent chains A and B overlap in a region of surface $\sim aN^{1/2}L$ (shaded area), L being the interface thickness.

In equation (16) we have used for L the expression $a \cdot \chi^{-1/2}$ [20]. The critical value of χ is then given by the usual three-dimensional expression :

$$\chi_c \sim \frac{1}{N}. \quad (17)$$

Since the two-dimensional value of χ_c is equals to the regular three-dimensional one, we expect equation (17) to apply for any three-dimensional system confined in one direction (molten polymer blend confined to a slab).

To our knowledge, no data are available at present on polymer blends in confined geometries. Long capillaries of circular cross-section can be realized in various ways, for instance in porous glass by leaching [21] or with open crystallographic structures such as zeolites [22]. It is to be hoped that future experiments will allow to check the predictions presented in this work.

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