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HAL Id: jpa-00210914
https://hal.science/jpa-00210914

LE JOURNAL DE PHYSIQUE

Short communication

Screening of interactions in polymer blends

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Résumé. — Dans cet article, nous étudions l'écrantage d'intéractions de mélanges binaires de polymères compatibles. Nous montrons que, avant d'atteindre la spinodale, il y a un point du type θ pour lequel le potentiel effectif est pratiquement nul et la chaîne se comporte comme une chaîne idéale. Nous établissons une expression générale du rayon de giration d'une chaîne dans le mélange en fonction de la concentration des deux composants et nous calculons le paramètre d'intéraction de Flory par la théorie des perturbations. Nous observons une réduction progressive depuis la valeur au-dessus de celle des chaînes gaussiennes idéales, jusqu'à la séparation de phase. Cette évolution est intéressante pour des expériences de diffusion neutronique dans la mesure où le facteur de forme d'une chaîne pourra être déterminé directement en fonction de la température (paramètre χ_F).

Abstract. — This paper discusses the screening of interactions in compatible binary polymer blends. It is shown that before the spinodal is reached a θ-like point exists, where the effective potential is essentially zero and the chain behaves ideally. A general expression for the radius of gyration of a single chain in the blend as a function of the concentration of the two components and the Flory interaction parameter is calculated by perturbation theory. This shows a progressive shrinking from a value above that of ideal Gaussian chains until the process reaches completion with the phase separation. This is of relevance in neutron scattering experiments, where the **single** chain structure

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factor of a single chain can be measured as a function of the temperature (χ_F-parameter) directly.

Introduction.

It was an old conjecture by Flory which suggested that the size of a single chain in dense solutions or melts is given by its Gaussian dimensions, i.e. $\langle R^2 \rangle = \ell^2 N$ [1]. ℓ is the effective step-length of the polymer chain and N the number of such Kuhn segments. This conjecture has been confirmed mathematically by Edwards [2], who introduced the concept of screening, and showed that excluded volume forces are screened by the presence of other chains at concentrations larger than an overlap concentration c^* [3]. The essential result is that in strong solutions the end to end distance of the chain is given by $\langle R^2 \rangle = \ell^2 N \{1 + v\xi/12c\}$, where v is the exclude volume parameter, c the concentration, and $\xi^2 = \ell^2/(12cv)$, i.e. the screening length, which determines the distance from which on excluded volume forces are screened, i.e. the blob size [3].

A similar situation is present in polymer blends, however the screening is more interesting since more than one kind of interaction is present and screening is problematic. The effective potential which acts on one chain is a delicate balance between the interaction parameters, which form the Flory χ_F parameter and the structure factor of this chain. We show that this effective potential changes sign before the phase separation takes place. This produces progressive contraction of the coil, which is completed at the phase transition. This should be possible to determine experimentally using neutron scattering experiments and selectively labelled chains [4]. Furthermore the phase separation as seen by a single chain can be studied, which is possible to study by computer simulation [5] on which we comment later.

Calculation of the screened potential.

As a simple example a binary polymer blend containing A and B species is considered. The partition function can be written in terms of functional integrals [6]

$$Z = \int \mathcal{D}\mathbf{R}(n) \exp\left[-3/(2\ell^2) \left\{ \int_0^{N_A} dn \mathbf{R}_A'^2 + \int_0^{N_B} dn \mathbf{R}_B'^2 \right\} \right.$$

$$- \int_0^{N_A} dn \int_0^{N_A} dn' V_{AA} \{\mathbf{R}(n') - \mathbf{R}(n')\} - \int_0^{N_B} dn \int_0^{N_B} dn' V_{BB} \{\mathbf{R}(n') - \mathbf{R}(n')\}$$

$$\left. - \int_0^{N_A} dn \int_0^{N_B} dn' V_{AB} \{\mathbf{R}(n') - \mathbf{R}(n')\} \right] \tag{1}$$

where N_A, N_B are the chain lengths of the A and B system respectively, n is the contour variable and $V_{\alpha\beta}$, $\alpha =$ A, B the appropriate interaction potentials between the A and B type monomers. Note that the notation in equation (1) is very short hand, because the integration on the variables **R** really include all chains present. In a mean field approximation the microscopic concentration fluctuations ρ_K^α of the component α ($\alpha =$ A, B) are treated as Gaussian variables and the partition function can be rewritten as [6]

$$Z = \int \prod_{A,B} \prod_k \mathcal{N}_k \, d\rho_{-k}^\alpha d\rho_{-k}^\alpha$$

$$\exp\left(-\frac{1}{S_{AA}^0(k)} \rho_k^A \rho_{-k}^A - \frac{1}{S_{BB}^0(k)} \rho_k^B \rho_{-k}^B - V_{AA}\rho_k^A \rho_{-k}^A - V_{BB}\rho_k^B \rho_{-k}^B - V_{AB}\rho_k^A \rho_{-k}^B \right)$$

$$(2)$$

where $S_{AA}^0(k)$ and $S_{BB}^0(k)$ are the unperturbed structure factors of the A and B system, i.e. $S_{AA}^0(k) = \langle \rho_k \rho_{-k} \rangle_0$ and $\langle \rangle_0$ is the unperturbed average. $\mathcal{N}_k$ is a normalisation factor which is not important for the considerations given here. In order to derive an effective partition function Z_A for the entire A system (including the effect of the B chains) we integrate the B system out ot get

$$Z_A = \int \prod d\rho_k^A d\rho_{-k}^A \exp\{-H_{AA}\} \tag{3}$$

where H_{AA} is the Edwards Hamiltonian, which can be written in density variables [6]

$$H_{AA} = \sum_k \left\{ \frac{1}{S_{AA}^0(k)} + V_{AA} - \frac{V_{AB}^2 S_{BB}^0(k)}{1 + S_{BB}^0(k) V_{BB}} \right\} \rho_k^A \rho_{-k}^A \tag{4}$$

This defines now the entire effective A system. But note that these chains are screened among themselves, and in order to find the final effective Hamiltonian for a typical A chain $\mathbf{R}_A(n)$ we have to integrate over all A chains except one. This procedure leads in a standard way [6] to

$$Z_A = \int \mathcal{D}\mathbf{R}(n) \exp\left\{ -3/(2\ell^2) \int_0^{N_A} dn \dot{\mathbf{R}}_A^2 \right.$$

$$\left. - \int_0^{N_A} dn \int_0^{N_A} dn' U_{AA}^S(\mathbf{R}(n) - \mathbf{R}(n')) \right\} \tag{5}$$

where

$$U_{AA}^{S} = \frac{V_{AA} + S_{BB}^{0}(k)\{V_{AA}V_{BB} - V_{AB}^{2}\}}{1 + V_{AA}S_{AA}^{0}(k) + V_{BB}S_{BB}^{0}(k) + S_{AA}^{0}(k)S_{BB}^{0}(k)\{V_{AA}V_{BB} - V_{AB}^{2}\}} \qquad (6)$$

which is the effective mean field potential (in k-space) produced by the blend acting on one A chain.

A few remarks can be made:

(i) if we take the special case $A \equiv B$, $V_{AA} = V_{BB} = V_{AB} = v$ we recover the screened potential derived by Edwards [2], i.e. $U_{\text{screened}} = v/(1 + vS(k))$;

(ii) we take treated the concentration fluctuations as Gaussian variables been careful not to impose an incompressibility constraint, such as $\rho_k^A = -\rho_{-k}^B$ for $k > 0$ and $\rho_o^A = -\rho_o^B = 1$ for $k = 0$. This can be done by taking the limit of very large repulsive potentials, i.e. we write for the potentials $V_{\alpha\beta} = V + \epsilon_{\alpha\beta}$, and take the limit $V \ll \epsilon_{\alpha\beta}$. The limit $V \longrightarrow \infty$ exists and we find

$$U_{AA}^{si} = \frac{1 - 2\chi_F S_{BB}^{0}}{S_{AA}^{0} + S_{BB}^{0} - 2\chi_F S_{AA}^{0} S_{BB}^{0}} \qquad (7)$$

with $\chi_F = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$;

(iii) it is worth noting that if we had used the incompressibility condition directly in equation (2) we would have recovered the usual random phase approximation (RPA) of de Gennes [3], i.e.

$$H_{RPA} = \left\{ \frac{1}{S_{AA}^{0}(k)} + \frac{1}{S_{BB}^{0}(k)} - 2\chi_F \right\} \rho_k^A \rho_{-k}^A \qquad (8)$$

for the entire A system. Employing now the screening calculation, i.e. integrating $N - 1$ A chains out the same result as equation (7) would have been found.

Discussion of the effective potential U_{AA}^{s}.

Let us discuss the incompressible AB system first. There are two important features in the effective potential in equation (7). The first one is a divergence at the condition

$$\frac{1}{S_{AA}^{0}(k)} + \frac{1}{S_{BB}^{0}(k)} - 2\chi_F = 0 \qquad (9)$$

which is de Gennes' celebrated equation for the spinodal which is for $k \longrightarrow 0$ identical to $\chi_0 - \chi_F = 0$, where $2\chi_0 = 1/(N_A \Phi_A) + 1/(N_B \Phi_B)$. Thus when χ_F approaches χ_0 the effective screened potential diverges. However, before the spinodal is reached the potential changes sign and becomes attractive when

$$1 - 2\chi_F S_{BB}^0 = 0 \tag{10}$$

or at the limit $k \longrightarrow 0$, we find

$$\chi_F = \chi_B \equiv 1/(N_B \Phi_B) \tag{11}$$

Whenever the interaction parameter exceeds the value χ_B the potential becomes attractive and diverges and at the spinodal $\chi_F = \chi_0$. This effect is clearly reflected in the size of the chain as we will show shortly. Before we go on to do this the spatial dependence of the screening potential equation (6) merits some attention.

Spatial dependence of the screened potential.

In order to simplify the algebra we consider a special symmetric case, i.e. $N_A = N_B = N, V_{AA} = V_{BB} = V$, and $V_{AB}^2 = V^2 - 2\chi_F V$, which contains already the important features. The structure factor can be approximated by [6]

$$S_{\alpha\alpha}^0(\mathbf{k}) = \frac{N\Phi_\alpha}{1 + q^2 \ell^2 N/12} \tag{12}$$

The spatial dependence of the screened potentials is then

$$U_{AA}^S(r) = 1/(2\pi)^3 \int d^3k \, U_{AA}^S(\mathbf{k}) \, e^{i\mathbf{kr}} \tag{13}$$

Using equation (14) the screened potential becomes

$$U_{AA}^S(\mathbf{k}) = \frac{K^4 - \Phi_B 2\chi_F K^2}{K^4 + V K^2 - 2\chi_F \Phi_A \Phi_A} \tag{14}$$

with the abbreviation $k^2 = (N^{-1} + k^2 \ell^2/12)$. The Fourier transform is straight forward and the final result for $V \gg \chi_F$ contains two Yukawa-type potentials

$$U_{AA}^s(r) = V \left(\delta(r) - \frac{\xi_1^2}{4\pi r} \exp(-r/\xi_1) + \frac{\xi_2^2}{4\pi r} \exp(-r/\xi_2) \right) \qquad (15)$$

with

$$\xi_1^2 = \ell^2/(6V), \xi_2^2 = \ell^2/\{\Phi_A \Phi_B (\chi_0 - \chi_F)\} \qquad (16)$$

and $\chi_0 = \Phi_A \Phi_B/N$. It is interesting to note that the contribution from the potential V and that from $\chi_0 - \chi_F$ have different sign. The first one is identical to that of the screening calculation of Edwards for the strong solution case [2] which does not depend on the composition of the blend, whereas the second one is that of de Gennes for the incompressible blend [3]. If we take the limit $V \longrightarrow \infty$ the classical case of the binary blend is recovered. At the particular value $\chi_F = \chi_B$, when U_{AA}^{si} becomes zero, the range ξ_2 of the attractive screening potential is given by

$$\xi_2^2 = \ell^2/\{\Phi_A \Phi_B (\chi_0 - \chi_B)\} \equiv \ell^2 N_A/\Phi_B \qquad (17)$$

i.e. the size of the A coil.

The size of a single chain in the binary polymer blend.

The effective Hamiltonian of the single chain can be written from equation (5) as

$$H_{\text{eff}} = 3/(2\ell^2) \int_0^{N_A} dn \mathbf{R}_A^{\cdot 2} + \int_0^{N_A} dn \int_0^{N_A} dn' U_{AA}^s \{\mathbf{R}(n) - \mathbf{R}(n')\} \qquad (18)$$

Here we to use the symmetric case as before. We have seen that the potential is positive (repulsive) for all k when $\chi_F < \chi_B$, i.e. the chain will be extended. At $\chi_F = \chi_B$ the potential will be zero and we will have an "ideal size" in the blend, very similar to the θ-point in solutions. As $\chi_F \longrightarrow \chi_0$, the screened potential becomes increasingly attractive and the chain "collapses" to an environment of A monomers at $\chi_0 \chi_F$. This effect can be studied by perturbation theory, since we work in a dense system and we do not have to worry about changing in critical exponents. We follow reference [6] for the calculation. The structure factors are approximated by equation (12) again.

The first order perturbation of the end to end distance is given for long chains (see [6]) for the symmetric case

$$\langle R^2 \rangle = N\ell^2 \left[1 + \frac{12}{\pi \ell^4} \int_0^\infty dk \frac{1}{k^2} U_{AA}^s(k) \right] \qquad (19)$$

It turns out that this integral is singular for $k \longrightarrow 0$. But note that comes from the fact that we used infinite long chains (compare the approximations in references [6]). This singularity can be removed by a (soft) cut off in the form

$$\int_0^\infty dk \frac{1}{k^2} U_{AA}^s(k) \longrightarrow \int_0^\infty dk \frac{1}{k^2 + N^{-1}} U_{AA}^s(k) \tag{20}$$

This simplifies the remaining integral and the final answer is given by

$$\langle R^2 \rangle = N_A \ell^2 \left[1 + \frac{12}{\pi \ell^4} \left\{ V^{1/2} + \frac{V}{N} \frac{1 - \Phi_B 2\chi_F N}{(\chi_0 - \chi_F)^{1/2}} \right] \tag{21}$$

which is our central result. The radius of gyration contains two terms. The first one is the classical result of Edwards [2]. The second one is the effect of the blend and indicates the "pre-transition" to a θ-type state. The chain is extended first, then it shrinks since the second term becomes negative. If the phase separation is approached the second term becomes negative, indicating a strong attraction. In this effective chain picture this means that the A chain is now surrounding itself in a environment of A monomers from other chains. It does not mean that the chain collapses to a size which is less than the appropriate size in the A environment. This limiting size is not contained in equation (21), since only first order the first order perturbation term has been calculated. Nevertheless we expect a significant effect on the radius of gyration arround the pre-transition, as we will discuss in the next section.

Discussion

We have presented a simple model of screening in a binary polymer blend and given an expression for the effective screening potential in the blend. This consists of two contributions : -the original found by Edwards [2] and another one of opposite sign with a range determined by $(\chi_0 - \chi_F)^{-1/2}$, i.e. the distance from the Flory interaction parameter from the spinodal. Calculation of the radius of gyration predicts a "pre-transition" before the phase separation is achieved when the coil assumes an "ideal" size. This should be seen in neutron experiments using selective deuteration for one species. It has been recently reported by a computer simulation that similar effects have been observed in polymer solutions which contain polymers in binary solvent [7]. This is a essentially a three component system. Nevertheless if the solution is not diluted and a similar mean-field approximation is applied one can treat the system in a similar way. That means if the variables of one solvent are integrated out, we are left with one chain in an "effective solvent", i.e. a solvent containing the effect of the other one on the chain. If (in dense solution) the polymers screen their interaction among themselves, we expect similar results, but with a more limited validity, since corrections to such mean-field results are expected to be stronger than in the blend.

Furthermore computer simulations in binary polymer blends give also indications for the pre-transition predicted here. Sariban and Binder [5] carried out an extensive numerical simulation of binary polymer blends. One of their result is the computation of the size of a particular chain in the blend as a function of the Flory χ_F parameter, i.e. the temperature. It is indicated from their simulation that the chain shrinks to values $\sim 15\%$ less than the original size, before the blend separates.

It is important to realize that this effect is not contained in the usual Random Phase Approximation and has to be considered as a higher order effect due to fluctuations. That means that the fluctuations which create the attractive part in the effective potential have higher order effects on the size of a polymer in a blend. Note that the fluctuations have been treated in a Gaussian approximation, which becomes invalide close to the phase separation point, i.e. near the spinodal decomposition higher order terms in the distribution of the concentration fluctuations have to be taken into account.

This theory applies to deformed systems as well if we use the deformed structure factor. The simplest approximation for the structure factor in deformed systems can be regarded as $S(\mathbf{k}, \lambda) \approx N_\alpha \Phi_\alpha / \left\{ 1 + (k\lambda)^2 N_\alpha \ell^2 / 12 \right\}$, where λ is the elongation factor of a single chain. In this case it predicts for the size of the chain

$$\langle R^2 \rangle = N\ell^2 \left(\lambda^2 + \lambda\Delta \right) \qquad (22)$$

where Δ is the effect of screening given by equation (21). More complicated models for the chain deformation provide different formulae, but the essential feature is already present in equation (22). A more elaborate theory of the deformation dependence will be content of an extended paper [8, 9].

Acknowledgments.

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