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Collapse of grafted chains in poor solvents

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Résumé. — On présente une théorie de champ moyen pour des chaînes greffées sur une surface en mauvais solvant. L'effondrement de chaînes greffées qui ne se recouvrent pas est identique à celui de pelotes libres, mais sans séparation de phase. Pour des couches greffées denses, cet effondrement fort, dans lequel le rayon R d'une pelote de N monomères passe de $R \sim N^{3/5}$ en bon solvant à $R \sim N^{1/3}$ en mauvais solvant, est remplacé par un effondrement « faible ». Dans cet effondrement « faible », la couche greffée s'amincit, mais les chaînes restent étirées même en mauvais solvant, et l'épaisseur de la couche reste linéaire en N. Pour des couches greffées peu denses, l'effondrement « faible » est couplé à une transition du premier ordre. Par accroissement de la densité de greffage le système passe par un point critique au régime d'effondrement graduel.

Abstract. — A mean field theory of the collapse of grafted chains (consisting of N monomers) in a poor solvent is presented. The collapse behaviour of nonoverlapping grafted chains is identical to that of free coils but with no phase separation. This « strong » collapse, in which the coil radius R decreases continuously from $R \sim N^{3/5}$ in a good solvent to $R \sim N^{1/3}$ in a poor solvent, is replaced by « weak » collapse for densely grafted layers. Such a layer when undergoing « weak » collapse becomes thinner, yet the chains remain stretched even in poor solvents, and the layer thickness is linear in N past the collapse. For low densities the « weak » collapse is associated with a first order phase transition. An increase in grafting density takes the system through a critical point into a gradual collapse regime.

1. Introduction.

The size of polymer coils varies with the quality of the solvent : the coils are swollen in good solvents and contract with diminishing solvent quality. Thus, the radius of free linear chains consisting of N monomers scales as $N^{3/5}$ in a good solvent, as $N^{1/2}$ in a θ solvent and as $N^{1/3}$ in a poor solvent — in the collapsed regime [1-3]. A similar general pattern is expected for polymers *attached to interfaces*. However, as the configurations of such polymers in good solvent differ significantly from those of free coils [4], one may expect a corresponding difference in their collapse behaviour [5]. Aside from the theoretical interest in polymer collapse, this problem is relevant both from an experimental point of view and to various practical applications. Because polymer collapse occurs simultaneously with phase separation, experiments on collapsed free coils are hindered by very low concentrations and fractionation effects [3]. Such difficulties may be avoided by the use of polymers irreversibly attached to a surface. Absorbed polymers are widely used to stabilize colloidal suspensions [4]. A change in solvent quality may then be used to induce flocculation. A better understanding of the resulting collapsed state may prove useful for such applications.

In the following we consider the *collapsed regime of grafted polymers* i.e., polymers attached to a surface by a headgroup only. Theoretical [6, 7, 8] and experimental [9, 10] investigations of grafted polymers were carried out for good and θ solvents. These suggest that for low grafting densities, such that the coils do not overlap, the chains behave essentially as free chains (Fig. 1a). For higher grafting densities, past the overlap threshold, the chains stretch in a direction normal to the surface. For high densities the layer thickness is linear in N (Fig. 1b). Little attention was, however, given to the behaviour of such systems in poor solvents. In our discussion of this case we consider linear chains which are *irreversibly* bonded to a *flat, solid* surface. The surface is

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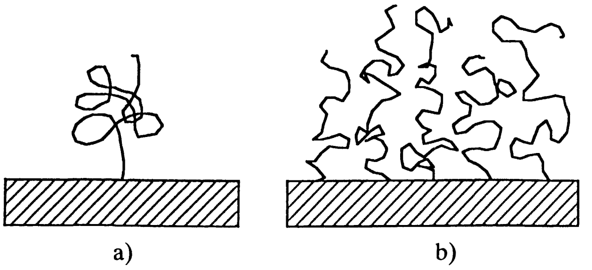

Fig. 1. — The configuration of the grafted chains in the : (a) low grafting density ($R_F > D$) regime (« mushrooms ») (b) high grafting density ($R_F < D$) regime (« cigars »).

taken to be *repulsive :* no adsorption is allowed except for the headgroup. We confine our discussion to *uncharged* polymers. For simplicity we assume the chains to be *monodisperse*. We base our analysis on a Flory type mean field approach. This method yields the correct dimensions of a grafted layer in a good solvent but overestimates its free energy. However, because the θ point is a tricritical point where mean field treatments are essentially valid, the Flory approach should be even better in the vicinity of the θ temperature. We follow the presentation of de Gennes [11] and of Williams *et al.* [3]. First we consider the low grafting density limit, where the average separation of grafting sites, D, exceeds the Flory radius, $R_F \approx N^{3/5} a$ (a = manomer size). The collapse behaviour in this limit is essentially that of free coils (« strong » collapse). This is due to the lack of interaction between the coils in this regime. We present this case for comparison purposes with the high grafting density regime, $D \ll R_F$, where significant modifications of the collapse behaviour occur. Specifically, we find that while the grafted layer is thinner in poor solvents, no « strong » collapse occurs : the grafted chains are stretched out in both good and poor solvents, and the layer thickness, L, is linear in N for both cases. The « weak » collapse which does occur is associated, for low enough grafting densities, with a first order phase transition. Because the densely grafted layer is not a finite system, the suggestion of such a phase transition is not as questionable as it is for the low grafting density regime.

2. Mean field theory of grafted polymers in poor solvents.

The free energy per chain, F, is assumed to consist of two terms : an elastic free energy, F_{el}, and a mixing free energy, F_{mix} :

$$F = F_{el} + F_{mix} \tag{2.1}$$

F_{el} accounts for changes in the coil configurational entropy due to deformations, assuming the chain obeys Gaussian statistics. F_{el} is given by

$$\frac{1}{kT} F_{el} \approx \alpha^2 - \ln \alpha \tag{2.2}$$

where α, the expansion factor, is defined by $\alpha = R/R_0$, R is the coil radius and R_0 the radius of an ideal coil. We aim to express F as a function of α and use α as a variational parameter. F_{mix} accounts for monomer-monomer and monomer-solvent interactions. Strictly speaking, F_{mix} of grafted chains differs from that of free coils. This is because the term reflecting the polymers translational entropy must be discarded once the coils are immobilized by the grafting. However, for the low concentrations of interest this is of no consequence. To obtain F_{mix} we integrate an appropriate free energy density, f_{mix}, over the volume occupied by the coil, V_{coil}. For a free energy density we use the following virial expansion [11] :

$$\frac{1}{kT} f_{mix} \approx c + \frac{1}{2} v a^3 c^2 + \frac{1}{6} w a^6 c^3 + \cdots \tag{2.3}$$

where c is the monomer concentration and v is the second virial coefficient. v is positive for high temperatures but changes sign at the θ temperature. In the vicinity of the θ temperature v may be written as

$$v = v_0 \frac{T - \theta}{\theta} \equiv v_0 \tau . \tag{2.4}$$

The third virial coefficient, w, is positive and temperature independent for the τ range of interest. w is related to the chain flexibility and may thus be varied by chemical modification of the polymer (change of side groups etc.). We now integrate f_{mix}, term by term, over the space occupied by the grafted coil. To do so we use the following mean field approximation :

$$\int_{coil} c^n \, d\underline{r} = \langle c^n \rangle V_{coil} \approx \langle c \rangle^n V_{coil} = \left(\frac{N}{V_{coil}} \right)^n V_{coil} \quad n = 1, 2 \ldots \tag{2.5}$$

where $\langle \; \rangle$ denotes average over the coil's volume.

So far our discussion applies equally well both to the high and the low grafting density layers. The two cases differ in the form adopted for V_{coil}. In keeping with common notation [7b] we have :

$$V_{coil} = \begin{cases} R^3 & D > R_F \\ D^2 L & D < R_F \end{cases} \tag{2.6}$$

where R is the radius of the isolated grafted chain and L is the thickness of the densely grafted layer. The crucial point is that *D is determined irreversibly by the grafting.* It is not self adjusting as are R and L.

As a result different powers of α appear in F_{mix} in the two limits

$$\frac{1}{kT}F_{\text{mix}} \approx$$
$$\approx \begin{cases} N + vN^{1/2}\alpha^{-3} + w\alpha^{-6} & D > R_{\text{F}} \\ N + vN^{1/2}(R_0/D)^2\,\alpha^{-1} + w(R_0/D)^4\,\alpha^{-2} & D < R_{\text{F}} . \end{cases} \quad (2.7)$$

In the high density regime ($D < R_{\text{F}}$), the expansion factor is defined by $\alpha = L/R_0$ and the inplane radius of the grafted chain is taken to be [7] R_0. Both F_{el} and F_{mix} are now given in terms of α. Our next step is to minimize F with respect to α.

In the low grafting density regime ($D > R_{\text{F}}$) we recover, as expected, the results obtained for free coils. The minimization of F leads to

$$vN^{1/2} = \alpha^5 - \alpha^3 - w\alpha^{-3} \qquad D > R_{\text{F}} . \quad (2.8)$$

The coil's radii for good ($vN^{1/2} \gg 1$) and poor ($vN^{1/2} \ll 0$) solvents are given by

$$R \approx \begin{cases} N^{3/5}\,\tau^{1/5}\,a & vN^{1/2} \gg 1 \\ w^{1/3}\,N^{1/3}\,|\tau|^{-1/3}\,a & vN^{1/2} \ll 0 . \end{cases} \quad (2.9)$$

Equation (2.8) predicts [11] a smooth crossover between the swollen ($\alpha > 1$) and the collapsed ($\alpha < 1$) regimes for $w > 0.038$. For $w < 0.038$ the solution develops an unstable branch: the free energy of the chain has two stable points suggesting a first order phase transition. However, as a single chain is a finite system this result is an artefact.

For the densely grafted layer ($D < R_{\text{F}}$) the minimization of the chain's free energy yields

$$vN^{1/2}(R_0/D)^2 = \alpha^3 - \alpha - w(R_0/D)^4\,\alpha^{-1} \qquad D < R_{\text{F}} . \quad (2.10)$$

This in turn leads to the following expressions for the layer thickness in good and poor solvents

$$L \approx \begin{cases} N\tau^{1/3}(a/D)^{2/3}\,a & vN^{1/2} \gg 1 \\ wN\,|\tau|^{-1}(a/D)^2\,a & vN^{1/2} \ll 0 \end{cases} \quad (2.11)$$

where the form of L in a good solvent conditions was already reported except for the τ dependence [12]. At the θ temperature we find

$$L \approx w^{1/4}\,N(a/D)\,a \qquad vN^{1/2} = 0 . \quad (2.12)$$

Our discussion of the dense regime is only valid for $L > D$. For lower L values the chains no longer overlap thus leading to low grafting density behaviour. Equations (2.11) and (2.12) reduce to the known single coil results for $L = D$. Note that in both regimes the dimensions of the collapsed coil are determined by the balance of two and three body interactions, with no contribution due to the chain's configurational entropy. On comparing equations (2.11) and (2.9) one should notice the diffent τ dependence in the two regimes. However, the remarkable aspect of the high density regime is the absence of « strong » collapse. While the densely grafted layer is thinner in a poor solvent, the grafted chains are stretched under all conditions. Furthermore, an analysis of equation (2.10) suggests the occurrence of a first order phase transition associated with this « weak » collapse (Fig. 2). The first order transition is predicted to occur for $w(R_0/D)^4 < 1/12$. A critical point occurs for $w(R_0/D)^4 = 1/12$, $vN^{1/2}(R_0/D)^2 = -11/12\sqrt{6}$ and $\alpha = (1/36)^{1/4}$. This prediction is free from the objection raised to the possibility of a phase transition in the low grafting density regime because we no longer deal with a finite system. Note that for the low grafting case, a change in the steepness of the configurational transition is accomplished by varying w. This entails chemical modification of the polymer. In the high density regime the relevant control variable is $w(R_0/D)^4$. Accordingly one may sample the phase diagram by changing the grafting density for a *single* polymeric species.

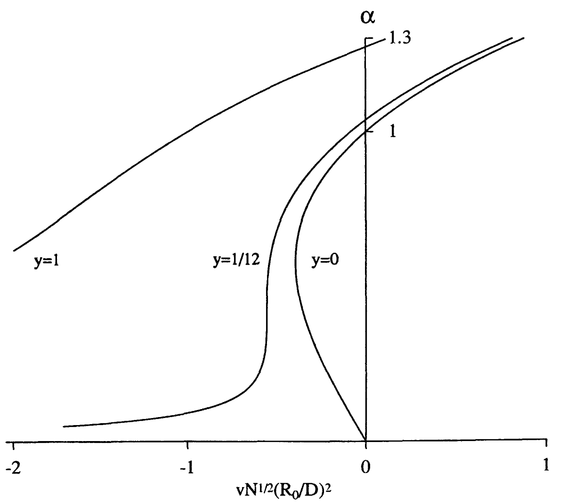

Fig. 2. — A plot of the expansion ratio α *versus* the reduced temperature $vN^{1/2}(R_0/D)^2$ for various values of $y = w(R_0/D)^4$.

3. Discussion.

Our analysis was based on a Flory's mean field approach. While this method yields correct scaling relations, a more sophisticated approach is needed in order to obtain the corresponding concentration profiles. Such investigations were recently carried out for densely grafted layers in good and θ solvents, using numerical methods [13] due to Scheutjens and Fleer [14] and Edwards type self consistent field methods [15]. In particular, the concentration profile of such grafted layers was found to be parabolic rather than flat as was previously assumed. A similar study of densely grafted layers in poor solvents is yet to be performed. For such systems one expects a concentration profile which is rather flat.

Within the Flory type picture, the collapse of sparsely grafted chains is identical to that of free coils. However, for grafted layers no phase separation can occur. It may thus be possible to use such systems in order to probe single coil collapse while avoiding problems associated with the phase separation : low concentrations and fractionation. Evanescent wave spectroscopy [16] may prove suitable for this purpose.

For densely grafted layers a new type of collapse behaviour is predicted. The « strong » collapse characteristic of free coils, which is associated with a dramatic decrease in coil size ($R \approx N^{3/5} a$ to $R \approx N^{1/3} a$), is replaced by « weak » collapse. In this last process the layer contracts with diminishing solvent quality, yet the chains remain stretched ($L \approx Na$) even for poor solvents. It is suggested that for sufficiently low densities past the overlap threshold, this « weak » collapse may take place as a first order phase transition. An increase in grafting density then shifts the system through a critical point to a regime where the collapse occurs gradually.

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