

Original Contributions

Collapse of polymer brushes induced by n -clusters

M. Wagner¹), F. Brochard-Wyart²), H. Hervet¹), and P.-G. de Gennes¹)

¹) Laboratoire de Physique de la Matière Condensée, Collège de France, France

²) Laboratoire de Physico-Chimie des Surfaces et Interfaces, Institut Curie, Paris, France

Abstract: Certain water soluble polymers may have a repulsive two-body interaction, but an attractive n -body interaction induced by certain “clustering” effects. In the bulk this may lead to a “ $\bar{\theta}$ point” in the phase diagram. Here, with polymer brushes, we construct the theoretical density profiles, using a local mean-field approximation. The brush often shows two layers (one dense near the wall, and one dilute), but the concentrations in both layers depend on the distance to the wall. The location of the interlayer boundary can be derived from a Maxwell construction.

Key words: Polymer brushes – poor solvents – chain conformation – phase separation

I. Introduction

In the standard Flory–Huggins [1] picture of polymer solutions the interactions are two-body interactions, described by a single parameter, the Flory χ parameter. When χ is small ($\chi < \frac{1}{2}$) monomers repel each other, the solvent is good, and the chains are swollen. At one particular point (the θ point) χ is equal to one-half and the chains are (nearly) ideal. At higher χ values phase separation occurs between a very dilute solution and a dense one.

Recently, a different scheme has been proposed, with special regard to water-soluble polymers [2]. Here, we may have solutions where two monomers repel each other, but a larger group of n monomers can build up a certain form of “cluster”. The thermodynamic phase diagrams are then greatly modified. In one regime, “ α ”, two dense phases coexist. In another regime, “ β ”, one dense phase is in equilibrium with a dilute phase. The limit between these two regimes is called the “theta bar” ($\bar{\theta}$) point.

Our aim here is to extend this discussion to polymer brushes. The more standard case of brushes near a classical theta point has been already considered by Halperin [3] and Zhulina [4]:

what was found here was a brush made of a single layer of the dense phase, with an abrupt drop in concentration at the outer end (Fig. 1a). In our case, for regime α , we expect two layers in the brush; one, close to the wall, is related to the denser bulk phase; the other (outer) layer is related to the more dilute bulk phase (Fig. 1b). The existence of these two layer structures may lead to some interesting interfacial structures.

Of course, the whole picture depends on very crucial assumptions: a) the whole approach of ref. [2], leading to a theta bar behavior, assumes that the “clusters” do not form ordered arrays (e.g., liquid crystalline phases): a certain chemical, or stereochemical disorder on the polymer backbone is probably required; b) we shall use a continuum description which assumes that the size of a cluster is very small when compared to the brush thickness. Thus, our discussion would not be relevant for short grafted chains; c) we allow the brush to show inhomogeneities only in the form of successive layers, i.e., the concentration profile $\phi(z)$ depends only on the distance z to the wall. In reality, things may be more complicated: the wall may be covered by patches of the dense phase (in some regular array), for the moment, we ignore these patchy structures.

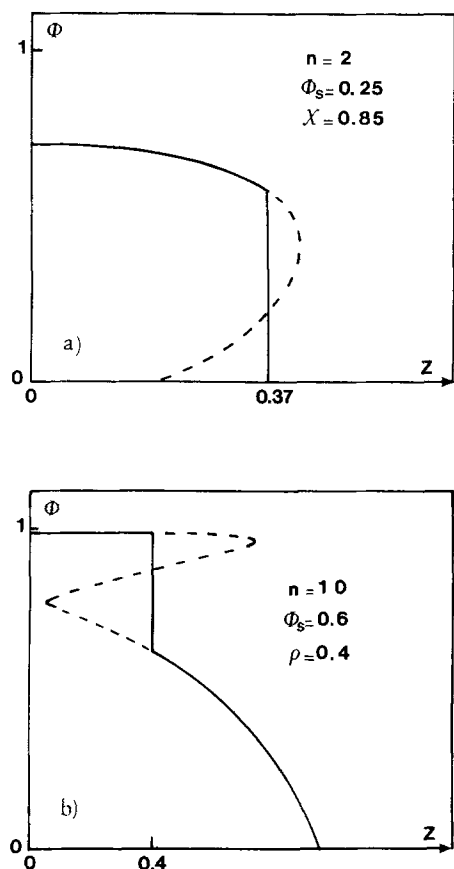


Fig. 1. Concentration profiles for a collapsed polymer brush a) in a usual “ θ ” solvent ($n = 2, \chi > \frac{1}{2}$); b) in a “ $\bar{\theta}$ ” solvent for regime α ($n = 10, \rho_c < \rho < \bar{\rho}$).

Starting with all these assumptions, we rederive the general theoretical background in section II: the main ideas follow Milner et al. [5], but we emphasize certain particular features of the discontinuities in $\phi(z)$.

In section III we present our results; section IV describes the main conclusions and some open questions.

II. Self-consistent field approach

A) General scheme

Our scheme follows the basic ideas of Edwards [6]. The successive monomers along one chain

(starting from the graft point) are labelled $1, 2, \dots, n \dots N$. Their positions are z_1, z_2, \dots, z_N . The mean-field free energy (divided by the thermal energy)

$$F = \sum_{\text{chains } 1}^N \int dn [F_{\text{el}} + F_{\text{int}}(\phi)], \quad (1)$$

where the elastic term has the (reduced) form^(*)

$$F_{\text{el}} = \frac{1}{2} \left(\frac{dz}{dn} \right)^2, \quad (2)$$

while the interaction term depends on the local concentration ϕ . For the one parameter cluster model of ref. [2]:

$$F_{\text{int}} = \rho_{(T)} (\phi - \phi^n) + (1 - \phi) \ln(1 - \phi). \quad (3)$$

Plots of $F_{\text{int}}(\phi)$ for various ρ values are given in Fig. (2). When $\rho > \rho_c = n^{-1}((n-1)/(n-2))^{n-2}$, two bulk phases are dense (regime α). If $\rho > \bar{\rho}^{**}$ one phase is dense and the other is dilute (regime β).

The effective potential acting on each monomer is the derivative of $F_{\text{int}}(\phi)$

$$\mu_{\text{int}} = \frac{dF_{\text{int}}}{d\phi}, \quad (4)$$

and the equation of local equilibrium (obtained by minimization of F) is

$$\frac{d^2z}{dn^2} = + \frac{\partial \mu_{\text{int}}}{\partial z}. \quad (5)$$

Milner et al. [5] show that the potential must be parabolic

$$\mu_{\text{int}} = A - Bz^2 \quad B = \frac{\pi^2}{8N^2}. \quad (6)$$

Equations (3) (4) and (6) lead to an implicit form of $\phi(z)$:

$$-n\rho\phi^{n-1} - \ln(1 - \phi) = B(h_m^2 - z^2), \quad (7)$$

where h_m is formally defined via $\phi(h_m) = 0$.

The constant A of Eq. (6) is the chemical potential μ_{int} at the wall, and is related to h_m by

$$A = Bh_m^2 + \rho - 1. \quad (8)$$

^{*}) In our reduced units, random walk step-length is unity.

^{**}) $\bar{\rho} = 1 - \exp(-n)$ for large n .

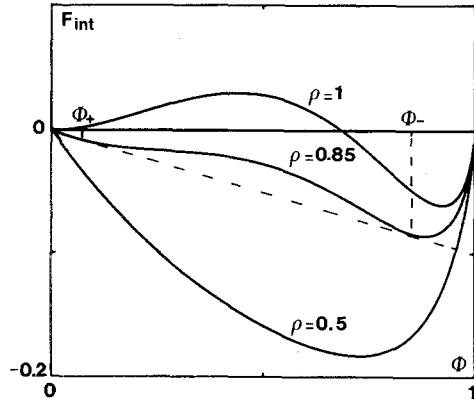


Fig. 2. Plot of the free energy $F_{\text{int}}(\phi)$ for $n=3$ and various ρ values: $\rho=0.5 (<\rho_c)$, $\rho_c < \rho=0.85 < \bar{\rho}$, $\rho=1 > \bar{\rho}$.

We eliminate the length N of the chains by introducing

$$\begin{aligned} Z &= \frac{z}{N} \\ H_m &= \frac{h_m}{N}. \end{aligned} \quad (9)$$

Physically, what is imposed is the total number of chains per unit area, which we call ϕ_s (in reduced units).

$$\phi_s = N^{-1} \int \phi(Z) dZ. \quad (10)$$

Computationally, rather than fixing ϕ_s , we choose a value of H_m , construct $\phi(Z)$ from Eq. (7), and determine the resulting ϕ_s .

B) Position of the interlayer boundary

In most cases of interest the profile $\phi(Z)$ derived from Eq. (7) is not single valued (Fig. 1b). This then shows the existence of a discontinuity: at a certain unknown location ($Z = H_1$) ϕ jumps from ϕ_- to ϕ_+ .

Near $Z = H_1$ the chemical potential of the solvent, or equivalently the pressure $\pi(\phi)$ of the polymer, is continuous: $\pi(\phi_1) = \pi(\phi_2)$. The pressure π has two components: osmotic and elastic,

$$\pi = \pi_{\text{os}} + \pi_{\text{el}}. \quad (10)$$

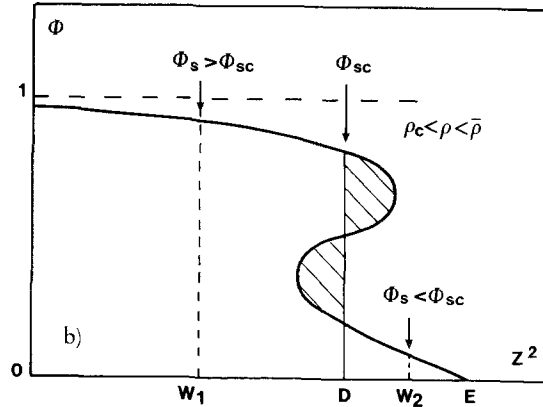
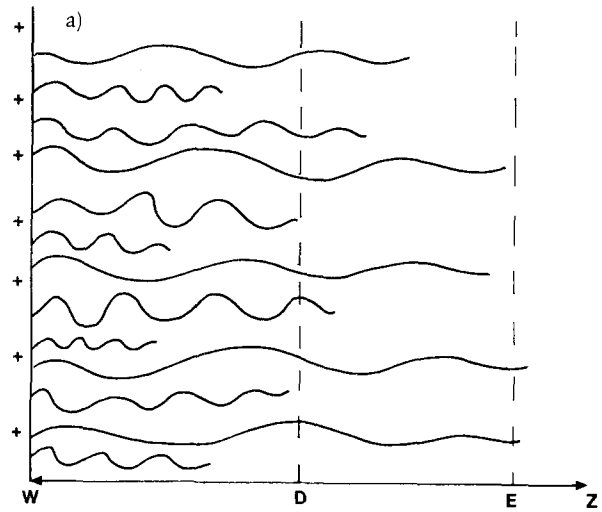


Fig. 3. Schematic representation a) of a copolymer brush, b) of the concentration profile versus Z^2 in the α regime. Points, E, D, W_1 , W_2 refer to the location of the end of the profile, of the discontinuity and two positions of the wall, respectively. All profiles for different grafting densities are superimposed, but W depends on ϕ_s . For $\phi = \phi_{sc}$, $W \equiv D$. For $\phi < \phi_{sc}$, the concentration profile is continuous ($W \in$ interval DE). For $\phi > \phi_{sc}$, W is to the left of D and two phases coexist.

We can divide the chains in two groups (Fig. 3a). The chains in group 1 cross the boundary, but their elastic deformation dz/dn is continuous [since $d\mu_{\text{int}}/dz$ is continuous in Eq. (5)]. Thus, for these chains $\pi_{\text{el}}(\phi_+) = \pi_{\text{el}}(\phi_-)$. The chains in group 2 have their ends on the plane $z = h_1$. For these chains, as explained by Milner et al., the elastic deformation vanishes $\pi_{\text{el}}(\phi_+) = 0$ and $\pi_{\text{el}}(\phi_-) \equiv 0$ by definition.

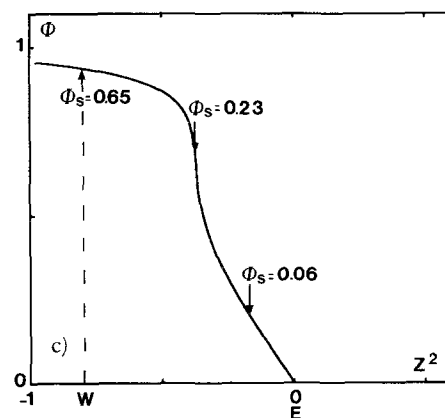
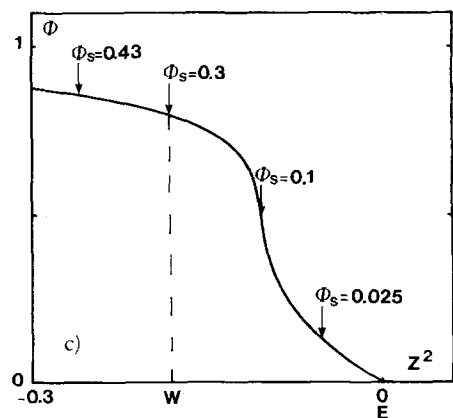
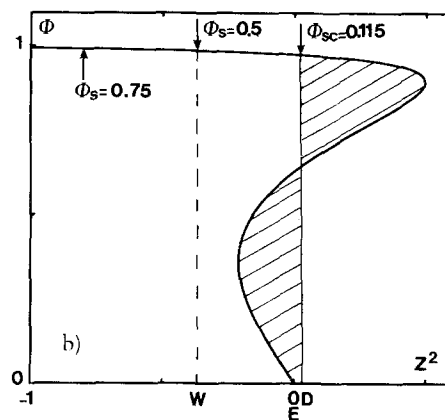
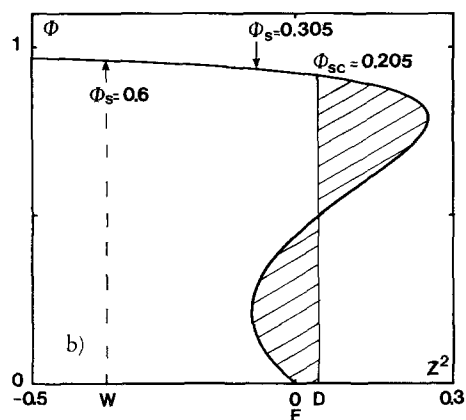
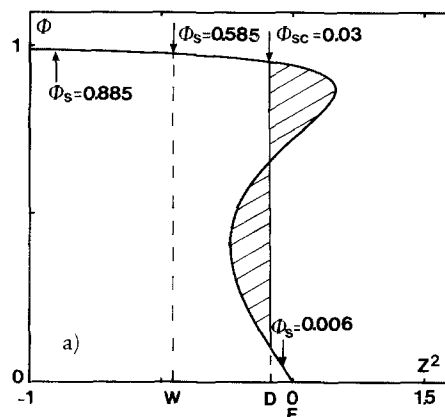
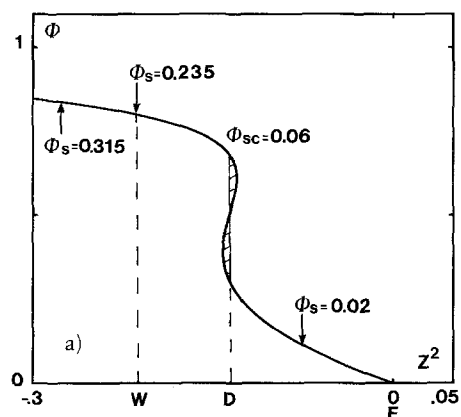


Fig. 4. Case $n = 3$: concentration profile ϕ versus Z^2 for different grafting density ϕ_s , a) in the α regime ($\rho = 0.7$), b) in the β regime ($\rho = 1$), c) in the swollen regime ($\rho = 0.64 < \rho_c$).

Fig. 5. Case $n = 4$: concentration profiles ϕ versus Z^2 for different grafting density ϕ_s for three typical ρ values a) $\rho = 0.85$; b) $\rho = 1$; c) $\rho = 0.54$.

Thus, the elastic tensions are continuous. Since the overall pressure π is continuous, the osmotic part π_{os} is also continuous:

$$\pi_{os}(\phi_+) = \pi_{os}(\phi_-). \quad (11)$$

On the free energy plot of the bulk solutions $F_{int}(\phi)$, this corresponds to the usual double tangent construction (Fig. 2). For our purposes, another construction is useful: if we plot the con-

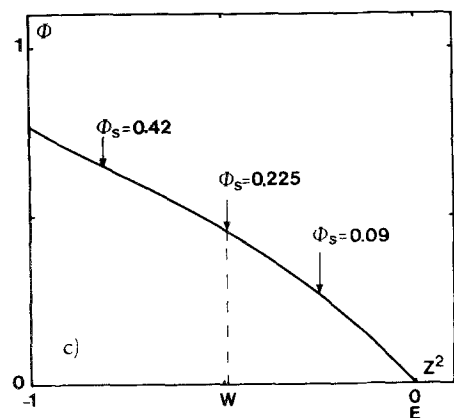
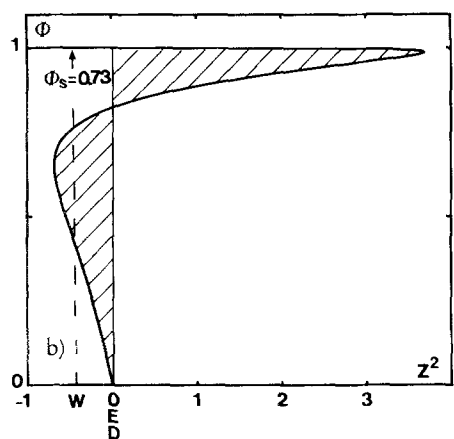
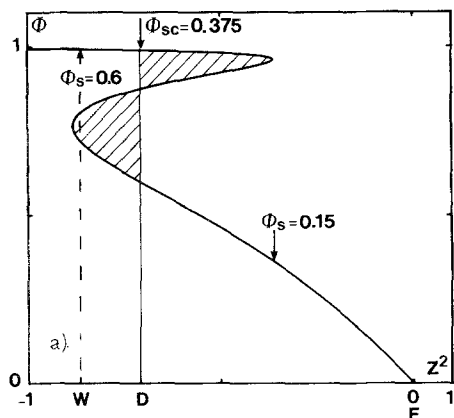


Fig. 6. Case $n = 10$: concentration profiles ϕ versus Z^2 for different grafting density ϕ_s for three typical ρ values a) $\rho = 0.4$; b) $\rho = 1$; c) $\rho = 0.24$.

centration ϕ , not as a function of Z , but as a function of μ_{int} [or equivalently of Z^2 , via Eq. (7)] we have a Maxwell construction of equal areas as shown in Fig. 4a. This construction simply ex-

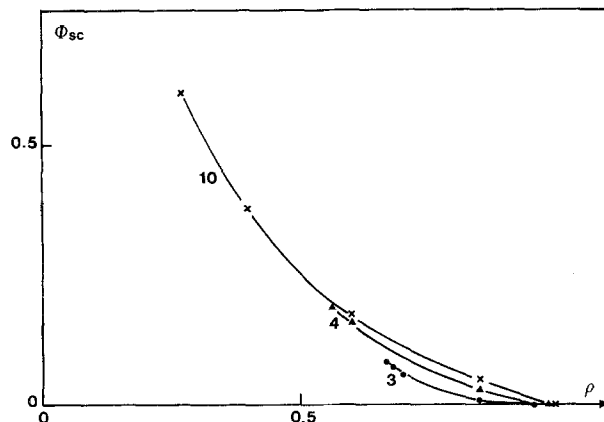


Fig. 7. Critical grafting density ϕ_{sc} versus ρ for $n = 10$, $n = 4$, $n = 3$.

presses the fact that μ_{int} and ϕ are conjugate variables for the bulk system. This is the construction which we use to locate the discontinuity.

III. Concentration profiles $\phi(Z)$ n, ρ, ϕ_s

As an example let us discuss the case $n = 3$ shown schematically in Fig. 3b and start with one particular ρ value $\rho = 0.7$. This is in the α -regime $\rho_c < \rho < \bar{\rho}$.

From Eq. (7) we can construct a plot of ϕ versus Z^2 (Fig. 4a). In this plot, three points are important:

- the end of the profile defined by $\phi = 0$ (point E);
- the location of the discontinuity point D derived from the equal area construction;
- the location of the wall (point W).

The whole plot is translationally invariant. It is convenient to fix point E, and to determine point W by Eq. (10), the conservation of the total number of monomers. All profiles for different grafting density in the representation $\phi(Z^2)$ are superimposed, but the origin (point W) depends on ϕ_s . For a critical grafting density ϕ_{sc} ($\phi_{sc} = 0.06$), points W and D coincide i) if $\phi < \phi_{sc}$, W is located in the interval DE: the brush is in a one-phase regime (the less dense phase) and the profile is continuous; ii) if

$\phi > \phi_{sc}$, W is to the left of D: the two phases coexist and the concentration profile is discontinuous. When ϕ_s increases towards unity, the concentration at the wall also approaches unity.

Let us now discuss another case $\rho = 1$ corresponding to the β -regime (Fig. 4b). The main difference is that now point E and D are in reverse order: the profiles now end at point with a discon-

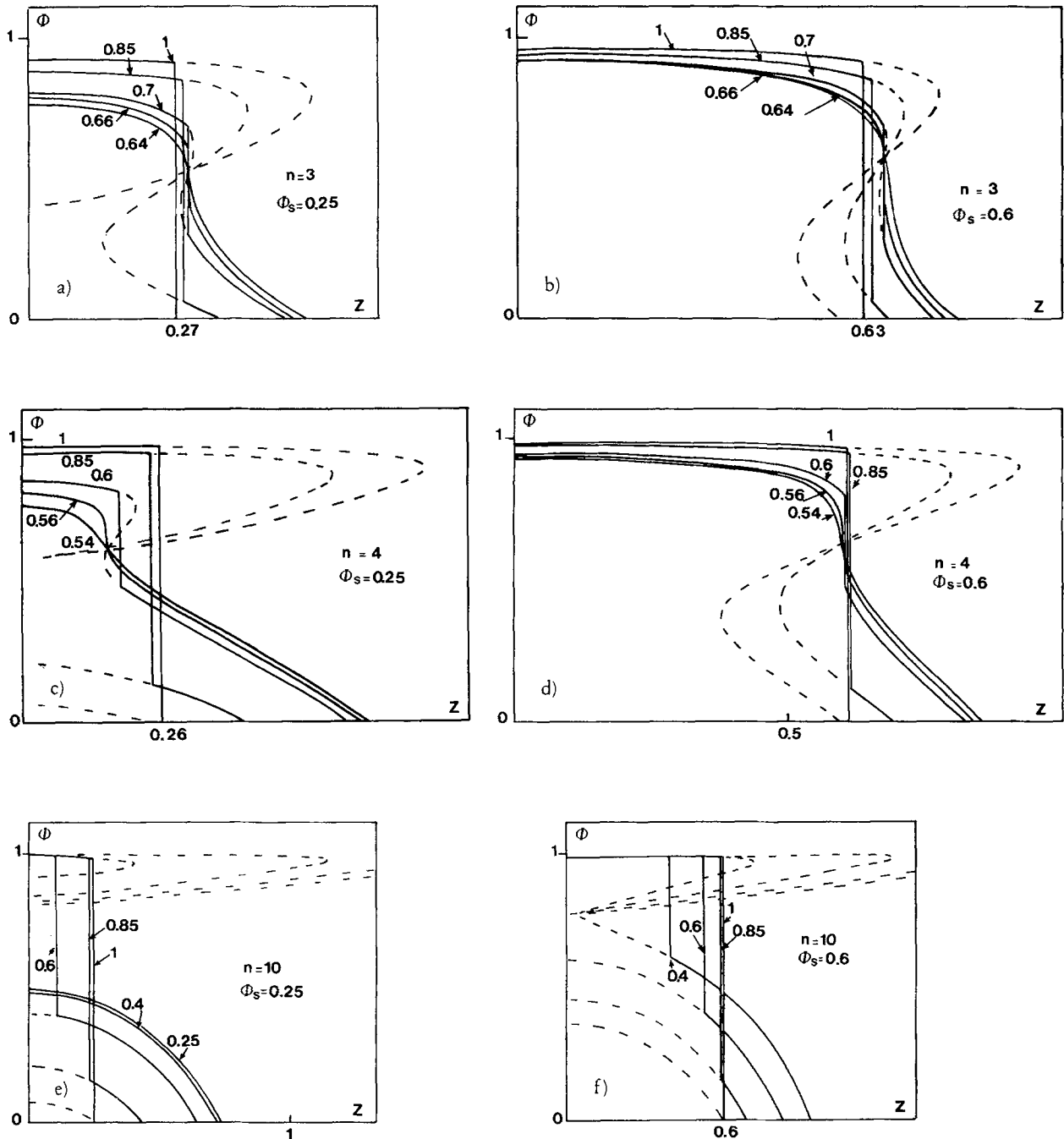


Fig. 8. Concentration profiles $\phi(Z)$ at fixed grafting density as a function of ρ (i.e., temperature) for three n values: a) $n = 3$, $\phi_s = 0.25$; b) $n = 3$, $\phi_s = 0.6$; c) $n = 4$, $\phi_s = 0.25$; d) $n = 4$, $\phi_s = 0.6$; e) $n = 10$, $\phi_s = 0.25$; f) $n = 10$, $\phi_s = 0.6$.

Table 1. Values of ϕ_{s_c} , ϕ_- , ϕ_+ , $H_m^2 - H_l^2$ as a function of ρ for $n = 3, 4, 10$.

n	ρ	ϕ_+	ϕ_-	$H_m^2 - H_l^2$	ϕ_{s_c}
3	0.6667 = ρ_c	0.48	0.48	0.156	0.085
	0.68	0.63	0.36	0.148	0.075
	0.7	0.68	0.29	0.136	0.060
	0.85	0.85	0.06	0.043	0.010
	0.9502 = $\bar{\rho}$	0.90	0	0	0
	1	0.91	0	-0.054	0
4	0.5625 = ρ_c	0.66	0.66	0.350	0.196
	0.6	0.82	0.48	0.315	0.160
	0.85	0.95	0.12	0.098	0.030
	0.9817 = $\bar{\rho}$	0.97	0	0	0
	1	0.97	0	-0.017	0
	10	0.2566 = ρ_c	0.89	0.89	1.060
0.4		0.98	0.61	0.730	0.375
0.6		0.98	0.40	0.412	0.175
0.85		0.98	0.15	0.132	0.05
0.99995 = $\bar{\rho}$		0.98	0	0	0
1		0.98	0	-0.0005	0

tinuity: the dense phase now coexists with pure solvent: this case is very similar to polymer brushes below the usual θ -point (Fig. 1a) as discussed in refs. [4] and [5]. The profiles $\phi(Z^2)$ are still superimposed and the origin (point W) is specified by ϕ_s as before.

Finally, for $\rho < \rho_c$ (Fig. 4c), the profile $\phi(Z^2)$ is continuous.

We show similar profiles for larger values of n , namely, $n = 4$ (Fig. 5) and $n = 10$ ($\rho_c = 0.256$) (Fig. 6). Values of ϕ_{s_c} , ϕ_- , ϕ_+ , $H_m^2 - H_l^2$ as a function of ρ for $n = 3, 4, 10$ are given in Table 1. Notice that ϕ_{s_c} is a decreasing function of ρ (Fig. 7) and that ϕ_{s_c} is much larger for $n = 10$.

All our concentration plots up to now gave ϕ as a function of Z^2 . In Fig. 8, we give the physical profile $\phi(Z)$ for different values of ρ (i.e., varying temperature), at fixed grafting density (fixed ϕ_s) for $n = 3, 4$, and 10.

IV. Concluding remarks

1) The novel feature brought in by cluster associations ($n > 2$) is the possibility of finding grafted layers with two distinct sublayers (in the α -regime): one dense, and one less dense. This segregation occurs although our chains are all chemically identical, and all of the same length.

2) For brushes in good solvents, the detailed "Edwards-Milner" picture of Eqs. (5, 6) is not

always necessary: all the scaling laws can be obtained from a simpler "Alexander-de Gennes" picture, where all chains are uniformly stretched, and a very compact argument of the Flory type is enough to find the layer thickness. One may wonder whether this Flory approach can be used for the present n -cluster problem, by allowing for two sublayers with different densities and different stretching levels. This turns out not to work; at the boundary plane between the two sublayers, the elastic pressure is then discontinuous, and this is not what we found in section II.

3) On the technical side, we should emphasize that the Edwards equations assume a stretching which is not too strong $dz/dn < a$ (the monomer size). At large surface coverings ($\phi_s \rightarrow 1$) this may be violated.

4) On the practical side, we do have polymer-solvent systems which seem to show n -cluster effects a) Acrylates and polyacrylates have hydrophilic groups which tend to cluster: for example, n -butyl methacrylate (PBMA) forms gels in n -decane [7]. The estimated T_c is 84.2°C, while $\bar{\theta}$ is slightly smaller [8, 9]. b) Polik and Burchard [10] showed (via light scattering) that the system PEO/water separates into a very dilute phase and a concentrated phase. Here, we might have $\bar{\theta} \sim 70^\circ\text{C}$ and T_c slightly higher.

An important case of PEO is colloid protection [11]. If, at the temperature of interest, the bulk system shows coexistence between the two dense phases, we expect stabilization to be more secure when the grafting density is low ($\phi_s < \phi_{s_c}$). In the opposite case, with a dense sublayer near the wall, the danger of establishing gel phases between two adjacent grains is increased: this might result in bridging and flocculation.

5) An interesting extension of the present thoughts would concern the behavior of adsorbed polymer layers in conditions where n -clusters can be relevant. Technically, this is a more difficult problem, because fluctuations are much larger in an adsorbed layer: in a grafted system, fluctuations are weak and mean-field is a good starting point. In adsorbed systems, mean-field is a poor starting point.

References

1. Flory P (1953) Principles of Polymer Chemistry, Ithaca, N.Y., Cornell University Press

2. de Gennes PG (1991) *CR Acad Sc Paris II* 313:1117
3. Halperin A (1988) *J Phys France* 49:547
4. Zhulina EB, Borisov OV, Pryamitsyn VA, Birshtein IM (1991) *Macromolecules* 24:140
5. Milner ST, Witten TA, Cates ME (1988) *Macromolecules* 21:2610
6. Edwards SF (1965) *Proc Phys Soc London* 93:605
7. Jelic LM, Nunes SP, Paul E, Wolf BA (1987) *Macromolecules* 20:1943
8. Diplomarbeit Uwe Sander Mainz (1984)
9. Brandrup J, Immergert EH (1989) *Polymer Handbook* John Wiley & Sons, New York, 3rd edition
10. Polik W, Burchard W (1983) *Macromolecules* 16:978
11. Napper DH (1983) *Polymerisation of Colloidal Dispersions*, Academic Press, NY

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Authors' address:

Professor Françoise Brochard-Wyart
Laboratoire de Physico-Chimie des Surfaces et Interfaces,
Institut Curie,
11 rue Pierre et Marie Curie,
75231 Paris Cedex 05-France.