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Compression induced phase transitions in PEO brushes: the n-cluster model

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Abstract. The compression of brushes of terminally anchored chain within the de Gennes n-cluster model is analysed. This model was developed for Poly(ethylene oxide) in water but may apply to other systems. Brushes described by this model exhibit discontinuous concentration profile associated with the coexistence of an inner dense "phase" and an outer, dilute, one. The compression induces growth of the dense, weakly compressible region. This, in turn, gives rise to distinctive force profiles associated with changes of slope. When the dilute region disappears, the compression of two brushes can give rise to a transient attraction.

PACS. 36.20.Ey Conformation (statics and dynamics) – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 82.70.Dd Colloids

1 Introduction

Surface treatments reducing protein adsorption and cell adhesion are of great importance to biomedical engineering and to biotechnology. They enhance the biocompatibility of applications as diverse as controlled release vehicles and artificial organs. Coating by poly(ethylene oxide), PEO, is, possibly, the best available treatment [1–3]. PEO, $(CH_2CH_20)_n$, a neutral, flexible and water soluble polymer, is also widely used as a colloidal stabiliser and viscosity modifier of water born systems. The behaviour of aqueous solutions of PEO, in bulk and at interfaces was thus extensively studied [4–6]. Yet, a complete theoretical interpretation of the experimental results is still lacking. A theoretical model for the behaviour of PEO solutions in water was recently proposed by de Gennes [7]. In the de Gennes "n-cluster" theory χ_{eff} is an increasing function of the monomer volume fraction, ϕ, when the mixing free energy is described in terms of a single Flory χ_{eff} parameter. This gives rise to a novel form of coexistence within brushes of terminally anchored chains. An inner, dense, region coexists with an exterior dilute region thus giving rise to a discontinuity in the concentration profile [8]. This article is concerned with the corresponding force profiles. In particular, the force profiles of brushes described by the n-cluster model when compressed by a flat, impenetrable, non adsorbing, bare surface. As we shall see, the n-cluster model leads to distinctive variations in the slope of the equilibrium force profile. These result from the compression induced shift in the relative weight of the "coexisting phases" within the brush. The effect arises because the dense phase is only weakly compressible. When the compression involves two brushes, this model suggests a qualitatively novel feature: the onset of adhesion when the dilute region disappears. This is also the case when the compressing surface is selectively attractive to the dense layer. Accordingly, force profiles obtained by utilising the Surface Force Apparatus (SFA) can be used as a diagnostic for the validity of this model. The predicted force laws are of interest for the interpretation of current SFA experiments involving PEO brushes and for the design of future experiments. Similar signatures may also occur in pressure-area curves obtained from film balance studies involving diblock copolymers incorporating a PEO block. This analysis is also of interest for the following reasons. First, while the n-cluster model was formulated for PEO it may well apply to a wider family of polymers whose solubility in water is due to hydrogen bonding. This includes, for example, Poly(N-isoproylacrylamide) [9]. The de Gennes model may also apply to solutions of polyacrilates in apolar solvents [8]. Second, force profiles measured by SFA are directly relevant to the understanding of the role PEO brushes in colloidal stabilisation and in the repression of protein adsorption [10,11].

The de Gennes model, as applied to brushes, is briefly described in Section 2. The presentation is based on the "Pincus approximation" [12]. This enables an analytic, albeit approximate, description of the n-cluster brush. In particular, it provides explicit expressions for the concentration profile of the brush. In addition, it yields simple force laws that characterise the compression of the brush in certain ranges. The compressed brush is discussed in Section 3. As was noted before, this discussion is limited to the case of a brush compressed by an impenetrable, non adsorbing, flat surface. The experimental situation is discussed in the final section. In it we consider,

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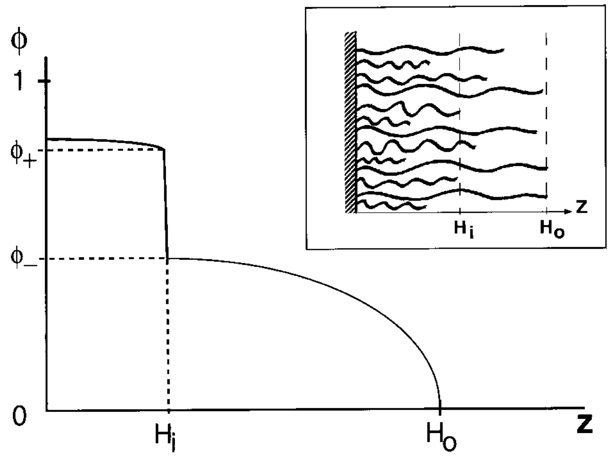

Fig. 1. A schematic concetration profile of an unperturbed n-cluster brush. It consists of an inner dense layer spanning the $0 < z < H_i$ region, and an exterior, dilute phase. The inset contains a schematic picture of the brush.

qualitatively, a number of pertinent issues: the compression of two brushes, the compression by a selective surface and the possible role of dynamics. As we shall see, the n-cluster model provides a possible rationalisation for the recent experimental results of Sheth and Leckband [10].

2 The n-cluster model: a brief summary

The de Gennes n-cluster model [7] is motivated by two experimental observations concerning the behaviour of PEO solutions in water. First, the effective χ_{eff} parameter, as obtained from calorimetric measurements, increases strongly with ϕ [4]. Note that this is the case when the mixing free energy is expressed in terms of a single Flory χ_{eff} parameter. Second, formation of aggregates at high ϕ [13]. It attributes this behaviour to attractive interactions involving clusters of $n > 2$ monomers while the binary interactions between monomers remain repulsive. Such higher order attractions may reflect, for example, formation of micelles or helices. Within this approach the attractive interactions between n monomers are described by a negative nth order virial coefficient, ρ. Following de Gennes we focus on the simplest case, of an athermal good solvent under dilute solution conditions *i.e.*, the second virial coefficient is $v = a^3$ where a is a typical monomer size. Accordingly, the Flory χ parameter, as defined by $v = a^3(1-2\chi)$, is $\chi = 0$. Attractive interactions leading to the formation of clusters of n monomers give rise to a $-\rho\phi^n$ term ($\rho > 0$) in the interaction free energy per unit volume, F_{int}. Altogether, F_{int}, in the limit of high polymerisation degree, $N \gg 1$, when the translational entropy of the polymer is negligible, is

$$F_{int}/kT = \rho(T)(\phi - \phi^n) + (1-\phi)\ln(1-\phi). \qquad (1)$$

The $\rho\phi$ term imposes $F_{int} = 0$ at $\phi = 1$ as is required from a mixing free energy. For $\rho > \rho_c = n^{-1}[(n-1)/(n-2)]^{n-2}$, F_{int} exhibits a concave, unstable region. This signals demixing into two bulk phases, dense and dilute, characterised respectively by ϕ_+ and ϕ_-. The values of ϕ_+ and ϕ_- at coexistence are determined by two conditions: (i) equality of the exchange chemical potentials, $\mu = dF_{int}/d\phi$ *i.e.*, $\mu(\phi_+) = \mu(\phi_-)$ and (ii) equality of the osmotic pressures, $\pi(\phi_+) = \pi(\phi_-)$, where $\pi = \phi dF_{int}/d\phi - F_{int}$. This amounts to the replacement of the concave region in F_{int} by a common tangent specified by

$$F_{int}(\phi) = \phi\mu(\phi_\pm) - \pi(\phi_\pm) \qquad \phi_- < \phi < \phi_+. \qquad (2)$$

The bulk demixing predicted for free PEO chains in water is qualitatively modified in a brush of terminally anchored polymers. Only the phase boundary survives, giving rise to a discontinuity in the concentration profile. The theoretical description of unperturbed PEO brushes within the de Gennes model was explored by Wagner *et al.* [8]. Their analysis involves a slight modification of the SCF method developed by Milner *et al.* [14] and by Zhulina *et al.* [15]. For brevity we use a simpler, approximate, argument, suggested by Pincus [12], to describe the results of Wagner *et al.* and to study the compression behaviour. The Pincus approximation occupies an inetermediate position between the Alexander model and the full SCF theory. It recovers the concentration profile as calculated using the SCF method. However, the approximation is based on an assumed form of the end point distribution. The assumed form differs from the one obtained *via* the SCF calcuation. The Pincus approximation can not thus replace the full SCF approach. However, its relative simplicity does allow one to obtain analytic, albeit approximate, experssions for the concentration profiles and the force laws. The flat brush, of uniform grafting density, σ, consists of monodispersed chains comprising each of N monomers. To ensure overlap between the chains, the area per chain, $\sigma^{-1}a^2$, is required to be smaller than R_F^2 where $R_F \approx N^{3/5}a$ is the Flory radius of the chain. The densely grafted layer is assumed to be laterally invariant. The mean free energy per unit area is $\gamma = \int F_{brush}dz$ where $F_{brush} = F_{int} + F_{el} - \lambda kT\phi(z)$ and z is the perpendicular distance from the surface into the solvent. The first term, F_{int}, allowing for the interaction free energy of the monomers, is given by (1). For the brush, this expression is valid for any N since the chains lose their translational entropy upon grafting. The treatment of the elastic free energy, F_{el}, is the core of the Pincus approximation. Two ingredients are involved: (i) each chain is considered as a Gaussian spring having a stretching penalty of $kTz^2/2R_o^2$ where $R_o \approx N^{1/2}a$ is the unperturbed chain span. This replaces the "local" elasticity used in the full SCF treatment. The chain ends are distributed throughout the layer with a density $\Psi(z)$. Altogether $F_{el}/kT = \Psi(z)z^2/2R_o^2$. (ii) $\Psi(z)$ is approximated by $\Psi(z) = const'\phi(z)/N$. This approximation is poor near the grafting surface, at $z \approx 0$. However, it yields the correct equilibrium conditions because of the dominance of highly stretched chains for which this approximation works well. Within this argument $const' = 1$ however comparison to SCF results suggests $const' = \pi^2/4$. The last term, $\lambda kT\phi(z)$, allows for the constraint on the number of monomers per chain and

λ is the corresponding Lagrange multiplier. The equilibrium condition $\delta\gamma/\delta\phi = \partial F_{brush}/\partial\phi = 0$ leads to $\mu[\phi(z)]/kT = \lambda - Bz^2$ where $\mu(\phi)$ is the local exchange chemical potential and $B = \pi^2/8N^2a^2$. At the outer edge of the unperturbed brush, $z = H_o$, $\phi(H_o) = 0$ and the equilibrium condition is thus

$$\mu/kT = B(H_o^2 - z^2) \tag{3}$$

where H_o is determined from

$$\sigma Na = \int_o^{H_o} \phi(z)dz. \tag{4}$$

Note that BH_o^2 is the exchange chemical potential at the grafting surface, $z = 0$. While $\rho < \rho_c$ the PEO brush is not expected to exhibit any exceptional traits. The signatures of the n-cluster model become apparent when $\rho > \rho_c$. In such cases it is possible to distinguish between three regimes. At low grafting densities, $0 < \sigma < \sigma_c$, the unperturbed brush is, essentially, described by a parabolic concentration profile. At higher grafting densities, $\sigma_c < \sigma < \sigma_u$, the concentration profile exhibits a discontinuity at the boundary between an inner, dense, region and an exterior, dilute one. Finally, when $\sigma > \sigma_u$ the brush comprises of a single, dense region. In order to obtain approximate expressions for σ_c and σ_u it is necessary to first consider the structure of the brush at the intermediate regime, $\sigma_c < \sigma < \sigma_u$.

The distinctive discontinuity in $\phi(z)$ as predicted by the n-cluster model appears when $\rho > \rho_c$. Its appearance is signalled by multiple roots to (3). These, in turn, are due to a van der Waals loop traced by $\mu(\phi)$ in the $\phi_- < \phi < \phi_+$ range. This behaviour is indicative of a concave, unstable region in F_{brush}. It suggests a coexistence between two phases, ϕ_- and ϕ_+. As we shall see ϕ_- and ϕ_+ are identical to those characterising the bulk coexistence. As before, ϕ_- and ϕ_+ are specified by two conditions: (i) $\mu_{brush}(\phi_-) = \mu_{brush}(\phi_+)$ where $\mu_{brush} = \partial F_{brush}/\partial\phi$ is the local exchange chemical potential at z. This leads to $\mu(\phi_+)/kT - Bz_+^2 = \mu(\phi_-)/kT - Bz_-^2$. Note that μ_{brush} includes a term reflecting the extension penalty of the chains. At the "phase boundary", $z_+ = z_- = H_i$ and $\mu(\phi_+) = \mu(\phi_-)$. (ii) $\pi_{brush}(\phi_+) = \pi_{brush}(\phi_-)$ where $\pi_{brush} = \phi^2[d(F_{brush}/\phi)/d\phi]$ is the local osmotic pressure. This condition reduces to $\pi(\phi_+) = \pi(\phi_-)$. Thus the coexistence within the brush involves the bulk monomer volume fractions, ϕ_+ and ϕ_-. However, because of (3) the coexistence is limited to a single altitude $z = H_i$ specified by

$$\mu(\phi_\pm)/kT = B(H_o^2 - H_i^2). \tag{5}$$

It thus appears as a discontinuity in $\phi(z)$. This argument indicates that the brush is described by F_{brush} with F_{int} in which the common tangent (Eq. (2)), replaces the concave region in the $\phi_- < \phi < \phi_+$ range.

For large n, $\phi_+ \approx 1 \gg \phi_-$ and it is possible to obtain an analytic approximation for $\phi(z)$ when $\rho > \rho_c$. In the range $0 \leq z \leq H_i$, where $\phi > \phi_+$, $\mu(\phi) \approx -\ln(1-\phi)$ and (3) leads to

$$\phi \approx 1 - \exp[-B(H_o^2 - z^2)] \approx 1 - (1-\phi_+)\exp[-B(H_i^2 - z^2)]. \tag{6}$$

When $\sigma \ll 1/a^2$, as is typically the case, $BH_o^2 \ll 1$ and (6) may be approximated by

$$\phi \approx \phi_+ + (1-\phi_+)BH_o(H_o - z). \tag{7}$$

At the outer range, $H_i \leq z \leq H_o$, where $0 \leq \phi \leq \phi_- \ll 1$, $\mu \approx 2\phi - n\rho\phi^{n-1} \approx \phi$ and (3) yields a parabolic profile

$$\phi \approx B(H_o^2 - z^2) \approx \phi_- + B(H_i^2 - z^2). \tag{8}$$

Once the brush structure in the $\sigma_c < \sigma < \sigma_u$ range is known we are in a position to estimate σ_c and σ_u. σ_c is attained when the maximal concentration in the parabolic brush, $\phi(0)$, equals ϕ_-. The dilute brush can not sustain higher concentrations. For $\sigma < \sigma_c$ the concentration profile is $\phi \approx B(H_o^2 - z^2)$ and $H_o \approx N\sigma^{1/3}a$. Accordingly $\phi(0) \approx BH_o^2 \approx \sigma^{2/3}$ and

$$\sigma_c \approx \phi_-^{3/2}. \tag{9}$$

The upper boundary of the coexistence range, σ_u, may be identified with the σ for which the brush consists of a single dense region such that at the outer edge $\phi(H_o) \approx \phi_+$. A rough approximation for σ_u is possible in the large n case when (7) is applicable. Arguing that $\phi(0) \approx 1$ leads to $H_o \approx Na$. The conservation of monomers condition leads to $\sigma Na \approx \int_o^{H_o} \phi dx \approx \phi(H_o)H_o$. Finally, the condition $\phi(H_o) \approx \phi_+$ yields

$$\sigma_u \approx \phi_+. \tag{10}$$

For $\sigma \geq \sigma_u$, all the monomers are incorporated into the dense region. This signals the breakdown of the Pincus approximation and the SCF theory. Both descriptions require the existence of a dilute, parabolic region at the outer edge of the brush. However, this requirement becomes unphysical for $\sigma \geq \sigma_u$ because this region is then fully depleted. This effect is due to the discontinuity in ϕ and it has no counterpart in "simple" brushes.

3 The compressed brush

For a give σ it is possible to move through these regimes by compressing the layer thus increasing the concentration within it. A dilute, parabolic brush will develop a "coexistence" profile upon compression to $H < H_c$. As in the case of σ_c, H_c is specified by the requirement $\phi(0) \approx \phi_-$. For a compressed brush, before the onset of coexistence, $\phi = \lambda - Bz^2$ and $\lambda \approx \sigma^{2/3}(H_o/H + H^2/H_o^2)$ where $H_o \approx N\sigma^{1/3}a$ [16]. Accordingly H_c is specified by

$$\phi_- \approx \sigma^{2/3}\left(\frac{H_o}{H_c} + \frac{H_c^2}{H_o^2}\right). \tag{11}$$

When $\sigma \ll \sigma_c$, $H_c \ll H_o$ and the first term is dominant. In this regime

$$H_c \approx \sigma^{2/3}H_o/\phi_- \approx \sigma Na/\phi_-. \tag{12}$$

Upon stronger compression, to $H < H_u$, the dilute region disappears and the brush is converted to a single dense region. The identification of H_u, as that of σ_u, is based on the requirement that $\phi(H_u) \approx \phi_+$. In the large n case, when $\sigma N a \approx \phi(H)H$, this leads to

$$H_u \approx \sigma^{2/3} H_o/\phi_+ \approx \sigma N a/\phi_+. \tag{13}$$

The compressive pressure, f, needed to maintain the brush at $H < H_o$ is equal to the osmotic pressure at the tip *i.e.,* $f = \pi[\phi(H)]$. $f = -d\gamma_{eq}/dH$ where γ_{eq} is obtained by integration of F_{brush} at equilibrium. At equilibrium $\mu/kT = \lambda - Bz^2$ and thus $F_{brush} = F_{int} - \phi\mu = -\pi$. Accordingly

$$f = \frac{d}{dH}\int_o^H \pi(z)dz = \pi(H) \tag{14}$$

where $\pi(z)$ is the local osmotic pressure. Since the compression of the brush always increases the concentration at the tip the force profile is monotonically increasing. This is in marked distinction to the familiar situations involving coexistence. For example, the compression of a fluid coexisting with its vapour is isobaric. In such situations the chemical potential of the two phases is identical. In the brush case this equality holds only at the discontinuity site. This consideration also leads to the immediate conclusion is that the compressive force at H_i, $f(H_i) = \pi(\phi_\pm)$, is independent of the grafting density. As we shall see, the force profile for $\sigma < \sigma_c$ exhibits three regimes. For weak compressions, $H_o > H > H_c$, the force profile of a "simple", parabolic brush is recovered. At intermediate compressions, $H_c > H > H_u$, the restoring force is weaker. This is an example of the LeChatelier principle. The restoring force when equilibration between the two phases is allowed is weaker than that expected in the absence of such internal degrees of freedom. Finally, for $H < H_u$ the force profile reflects the weak compressibility of the dense phase.

Simple expressions for the compressive force law are easily obtained in the vicinity of H_c and H_u. It is most convenient to consider the case of $\sigma < \sigma_c$ when $H_o \approx N\sigma^{1/3}a$ and $B \approx \sigma^{2/3}/H_o^2$. As was noted earlier, for weak compression, $H_o > H > H_c$, we expect the force profile of a parabolic brush. Within the Pincus approximation, ignoring numerical prefactors, we obtain [16]

$$\phi(z) \approx \sigma^{2/3}\left[\frac{H_o}{H} + \frac{H^2}{H_o^2}\right] - \sigma^{2/3}\frac{z^2}{H_o^2}. \tag{15}$$

Accordingly, the leading terms for $f/kT \approx \phi^2(H)$ are

$$f/kT \approx \sigma^{4/3}\left[\left(\frac{H_o}{H}\right)^2 - \left(\frac{H}{H_o}\right)\right]. \tag{16}$$

Here, and in the remainder of this section, we delete higher order terms since the Pincus approximation does not yield the correct expressions for them. When $H = H_c$, a dense phase begins to form. Thus, for $H_u < H < H_c$ it is necessary to allow for the effect of the coexistence. To this end, we utilise the relationship [17]

$$\phi_- - \phi = B(H^2 - H_i^2). \tag{17}$$

At the immediate vicinity of H_c, $H \leq H_c$, a thin dense layer appears. In this regime $H \gg H_i \approx 0$. Accordingly

$$\phi \approx \phi_- - \sigma^{2/3}\left(\frac{H}{H_o}\right)^2. \tag{18}$$

and the leading terms in f are

$$f/kT \approx \phi_-^2 - \phi_-\sigma^{2/3}\left(\frac{H}{H_o}\right)^2. \tag{19}$$

On the other hand, in the neighbourhood of H_u, $H \geq H_u$, the dense phase incorporates most of the brush. In this case, $H_i \approx H_u$ and thus

$$\begin{aligned}\phi &\approx \phi_- - \sigma^{2/3}\left[\left(\frac{H}{H_o}\right)^2 - \left(\frac{H_u}{H_o}\right)^2\right] \\ &\approx \phi_- - \sigma^{2/3}\frac{H_u}{H_o}\left(\frac{H - H_u}{H_o}\right)\end{aligned} \tag{20}$$

and

$$f/kT \approx \phi_-^2 - \phi_-\sigma^{2/3}\frac{H_u}{H_o}\left(\frac{H - H_u}{H_o}\right). \tag{21}$$

As was already discussed, the H dependence of (19) and (21) is indeed weaker than that exhibited by (16). One may attempt to obtain a more complete expression for f by utilising the conservation of monomers in addition to (17). This is beyond the scope of the present work, especially in view of the expected role of hysteresis in the problem. This effect, to be considered in the following section, may prevent the measurement of the equilibrium force law.

4 Concluding remarks

The reported force profiles [18,19], as obtained by SFA experiments involving PEO brushes, do not display the signatures of the n-cluster model, as analysed in this article. This may be due to a number of reasons. It is possible that the n-cluster model does not apply to PEO. As noted above, this model was motivated, in part, by reports of aggregation of PEO chains leading to gel like phase [13]. This observation is subject of debate [20,21]. At this point it is important to note the n-cluster model may apply to other systems. A promising candidate is Poly(N-isoproylacrylamide). Experimental data concerning brushes of this polymer was already interpreted in terms of the de Gennes model [9]. It would be thus interesting to study the compression behaviour brushes of Poly(N-isoproylacrylamide) using the SFA.

One should also consider the possibility that the n-cluster model does apply to PEO and that the expected force laws were not observed because of experimental difficulties. Two such difficulties come to mind. First, the values of $\rho(T)$ and n or, equivalently, ϕ_+ and ϕ_-, that characterise PEO are not known. It is thus impossible to predict the range of grafting densities and compressions where the effect is expected. This calls for a systematic study of PEO brushes over a wide range of grafting densities. However, for the systems studied [18,19], it is difficult to attain the range of interest *i.e.,* grafting densities beyond weak overlap. Second, one should consider the role of equilibration dynamics in these experiments. The calculated force profiles are based on the assumption that the compressed layer fully attains its equilibrium state. However, the distinctive features of the force profiles result from the occurrence of a compression induced first order phase transition. One should allow thus for potentially long lived metastable states. These will exhibit the behaviour of a "normal brush" *i.e.,* a brush having no attractive high order interactions. In turn, this suggests that the rate of compression is important. It might be necessary to maintain the layer at a state of compression for extended period in order to observe the predicted behaviour. This argument also suggests that the force profiles may exhibit hystersis effects. In particular, the decompression and compression curves may differ. Here, two contributing factors come into play. In addition to the possibility of long lived metastable state, the dense state is expected to have longer relaxation times. In fact, de Gennes [7] suggested that the marked hystersis observed in SFA experiments involving uniformly adsorbed PEO [22,23] may be due to the formation of a dense phase in the compressed layer.

Thus far we have limited the discussion to the situation analysed in this article, namely the confinement of the brush by a bare, non adsorbing plate. With certain important caveats, the predicted force laws are also valid for the compression of two brushes. The two situations are effectively indistinguishable so long as the dilute regions in the brushes survive. This is due to the limited interpenetration between the two layers [24,25]. However, qualitatively new features are expected when the dilute layer disappears. Two scenarios come to mind. One occurs when the grafting density is high enough, $\sigma > \sigma_u$, such that the uncompressed brush consists solely of a dense region. In this case one may expect the two layers to experience short range attraction. This is somewhat reminiscent of the attraction between polymer layers in a poor solvent [26]. However, in the poor solvent case the attraction is due to binary monomer-monomer interactions while within the de Gennes model it is due to the formation of "mixed" n-clusters, incorporating monomers belonging to the two brushes. Furthermore, in a poor solvent one expects attraction irrespective of the grafting density or even the adsorption mode. In the present scenario brushes display a transition from repulsion to attraction when the grafting density changes while immersed in an athermal good solvent. The second scenario occurs when the dilute region disappears because of strong compression, $\sigma < \sigma_u$ and $H < H_u$. In this case the initial interaction, while $H_o > H > H_u$, is expected to be purely repulsive. However, when the dilute "phase" disappears the two layers are expected to exhibit transient but possibly long lived attraction. In this, second, scenario the onset of the attraction may be slow because of the metastability issue discussed earlier.

Sheth and Leckband [10] recently reported SFA measurements of the interactions between a surface bearing grafted PEO chains and a surface bearing grafted proteins. Their essential results are as follows. At low compressive loads the interactions were repulsive and the resulting force curves were consistent with the theoretical predictions assuming that PEO behaves as a "simple" flexible chain. Attractive interactions developed when the compressive loads were higher. The nature of the PEO layer changed following such strong compression. A much weaker compressive load was necessary in order to achieve adhesion. This "modified form" of the PEO relaxed back to its "repulsive" form after a few hours. No deviations from the "simple chain" behaviour were observed when the compressive surface was coated by a lipid monolayer. The reported results are difficult to rationalise within the framework of standard polymer theory *i.e.,* considering flexible, structureless coils with positive virial coefficients. However the results are not inconsistent with the n-cluster model if one assumes that the interaction between the surface functionalities of the protein and the PEO n-clusters are attractive. Such interactions can, arguably, nucleate the dense PEO phase as well as give rise to contact attraction. The protein coated surface, within this discussion, is an example of a selective surface that is attractive only to the dense phase.

It is clear that the reported attraction between compressed PEO brushes and proteins does not prove that the n-cluster model indeed applies to PEO. These results are also not inconsistent with the theory of Bjorling *et al.* [27] which is based on very different assumptions. In particular it is assumed that monomers may interchangeably assume either a hydrophobic or hydrophilic state. This model also predicts dense brushes consisting of two regions. In this case the inner, dense, region is hydrophobic while the outer dilute region is hydrophilic. However, within this model the associated concentration profile is continuous. A similar behaviour is also expected within the model proposed by Bekiranov *et al.* [28]. In this model the ϕ dependent χ parameter reflects two contributions. The bare back bone is hydrophobic and thus experiences poor solvent conditions. This is however modified by Hydrogen bonds with the surrounding water molecules. These render PEO soluble so long as ϕ is low enough to allow a siginificant number of H-bonds. At this point it is impossible to grade the relative performance of the three models. It is nevertheless encouraging to note that the n-cluster model can provide an explanation for the experimental results discussed above. Clearly, considerable amount of experimental and theoretical work will be necessary in order to understand the behaviour of these systems.

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16. The conservation of monomers requirement $\sigma N = \int_o^H \phi dz$ leads to $\sigma N = \lambda H - BH^3/3$ or $\lambda \approx \sigma N/H + BH^2/3$.
17. The exchange chemical potential at the tip of the compressed brush is $\mu(\phi) = \lambda - BH^2$. At the site of the discontinuity $\mu(\phi_\pm) = \lambda - BH_i^2$. While $H > H_u$, the exterior of the brush is dilute, $\mu(\phi) \approx \phi$ and $\mu(\phi_\pm) \approx \phi_-$ thus yielding (13).
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