Polymer Gels and Brushes at Surfaces

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Summary: We discuss the adsorption of polymer gels on flat surfaces. Even in cases of complete wetting, where the spreading power S is positive and where an equivalent liquid would spread, the elastic stresses due to the gel deformation upon adsorption oppose spreading. The competition between elasticity characterized by the bulk shear modulus G and capillarity, characterized by the spreading power S, defines a typical length scale $\mathtt{l} = S/G$ for the deformation in the gel. Macroscopic gels larger than $\mathtt{l}$ deform only at their edges over a region of size $\mathtt{l}$. Microscopic gels show a finite deformation despite the elastic stresses. These results can be compared to confined polymer brushes.

Keywords: adsorption; gels; solvent spreading; surfaces; wetting

Introduction

The equilibrium structure of an adsorbed linear chain results from the interplay between the entropy loss due to confinement of the chain at the surface and the energy gain of the adsorbed monomers.[1,2] In a scaling description, an isotropic chain of contour length N, at the adsorption threshold has $N_s \sim N^{\phi}$ monomers at the surface with ϕ the crossover exponent. The chain adsorbs when the free energy gain $N_s\delta$ is larger than the thermal energy k_BT; here δ is the free energy gained upon contact of a monomer with the wall.[2,3] This sets the crossover to adsorption at N=g where $\delta g^{\phi} = k_BT$. An adsorbed chain still remains isotropic at a local scale D corresponding to the confinement thickness. A sub-chain of contour length g and size D=$g^{\nu}b$ (where $\nu \sim 3/5$ is the swelling exponent) is at the adsorption threshold and thus the adsorbed chain thickness is $D \sim b(\delta/k_BT)^{-\nu/\phi}$. For an impenetrable wall ϕ is close to ν. The free energy gain per adsorption blob of contour length g and area $1/D^2$ is of order k_BT. When adsorption proceeds from a solution,[4] a concentration profile develops that extends over one bulk correlation length. However, close to the wall, the layer can be viewed as a close packed array of adsorption blobs of size D, the proximal layer. Provided that D is smaller than the bulk

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correlation length, the reduction in surface tension with respect to pure solvent is dominated by this proximal layer and $\Delta\gamma \sim - k_BT/D^2$. For strong adsorption $\delta \sim k_BT$ and D becomes of the order of the monomer size b. The gain in surface tension is then of order k_BT/b^2. The corresponding problem for branched chains, microgels and gels is less well understood. Several works describe adsorption of polymers with various architectures from solution at the mean-field level.[5] In first attempts one of us has constructed a scaling approach to a first understanding of adsorption of branched structure.[6] There the solution suffers from the assumption of penetrable surfaces. We also studied the confinement of a finite brush[7] where edge effects somewhat similar to those in adsorbed gels occur.

The spreading of simple liquids between a surface and say, air, occurs when the spreading parameter $S = \gamma_{air/wall} - \gamma_{liq/wall} - \gamma_{liq/air}$ is positive. A drop then spreads to form a very thin film. The thickness of the film is fixed by the long range van der Waals interactions described by the relevant Hamaker constant A. The film thickness h is constructed from the spreading coefficient and the Hamaker constant, $h \sim (A/S)^{1/2}$.

Preliminaries and General Considerations

The adsorption behaviour of gels is mainly determined by the gain of energy under surface contact, i.e., the spreading of the gel on the surface. This spreading, however, is limited by the elastic properties and the deformation of the gel close to the wall. We shall see below that the size of the gel is another important factor, which determines the general physical behaviour.

In some respects, gels and their behaviour on surfaces may also serve as qualitative models for more complex mesoscopic elastic objects such as encountered in biology, which may tentatively be described by a shear modulus (or two elastic moduli). In the case of interest the corresponding uncross-linked polymer would adsorb at the interface and spread. It may be a molten polymer (in the case of a dry gel) or a polymer solution (in the case of a gel immersed in a solvent bath, the spreading parameter is then $S \sim k_BT/b^2$).

We first start with a qualitative discussion of dry gel deformation upon adsorption. For this purpose it is sufficient to consider the gel as an elastic medium characterized by one elastic constant, the shear modulus G and set the Poisson modulus σ to the value 1/2 for convenience at this stage. A typical length scale of the system is given by $\ell \propto S/G$. This length scale is constructed dimensionally by comparing the two important parameters, the spreading parameter S and the modulus G. It is the only intrinsic length scale of the problem. Therefore, the typical displacement of any point inside the gel upon adsorption is ℓ. We use the simple geometry illustrated in Figure 1. The form of the gel is assumed to be a half cylinder of (large) size l and diameter R.

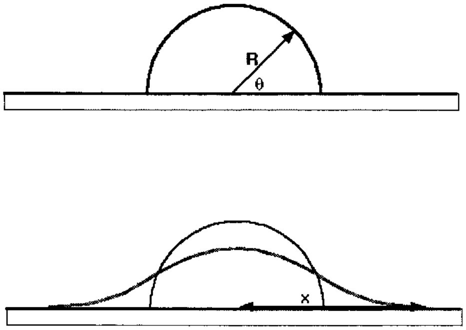

Fig. 1 The choice of the geometry of the sample for an effective two dimensional calculation. After applying the deformation, the semicircle will be deformed as indicated by the grey line. The change in height and length should be related to the scale $\ell \propto S/G$.

To be more specific, let us consider first a macroscopic half-cylinder of a gel with length l and of radius R on a surface as sketched in Fig. 1 (the results would be identical for a spherical gel of size R). Positive values of the spreading parameter S allow a spreading of the polymer gel on the surface. Then, close to the surface, the gel spreads and deforms to some extent with a typical displacement and forms a "foot" of extension ℓ. The typical deformation can be estimated as ℓ/R, and the associated elastic free energy is

$$F \propto G(\ell/R)^2\, V \qquad (1)$$

where V is the total volume of the gel. At the foot the deformation is of order 1 and thus the elastic free energy of the edge is

$$F \propto G\cdot 1\cdot \ell^2 l \qquad (2)$$

The gain in surface energy, of the order of $\Delta F = S\ell\, l$, is stored in the form of elastic energy: a finite fraction in the foot and the remainder in the bulk of the gel. There is also an increase in the contact area between the gel and the surrounding medium by about ℓL. This we want to neglect (it should not influence the shape of the gel). Consistency requires that the corresponding surface tension be negligible with respect to S. The inflexion point of the profile is located a distance $\sim R\theta$ from the surface with $R\theta^2 \sim \ell$ ($\theta < 1$). The maximum slope may be used to define a macroscopic contact angle $\psi \sim \pi/2-\theta$.

In addition, we remark that the elastic length ℓ can be of macroscopic order. If we use the rather general form of the gel modulus for unentangled gels $G \sim k_BT$ per cross-link, and if we further assume, for simplicity, that the gel is at maximum swelling at the overlap concentration of the elastic chains c^*, the shear modulus is of the order of $G \sim k_BT/\xi_p^3$, where $\xi_p \sim b\ N^{\nu}$, N being the number of monomers between two cross-links and b the monomer size. As argued above, the spreading parameter S is determined mainly by the scale of the monomers b, i.e., $S \sim k_BT/b^2$. Therefore,

$$\ell \approx \xi_p \left(\frac{\xi_p}{b}\right)^2 \sim bN^{3\nu} \qquad (3)$$

The elastic length increases sharply with the molecular weight of the chains and becomes large for weakly cross-linked gels. For dry gels (rubbers) synthesized in the melt, the modulus is dominated by trapped entanglements, $G \sim k_BT/N_eb^3$, with N_e the entanglement length. ℓ then becomes shorter by the order of 10 nm.

If ℓ is small, van der Waals forces may become important and thicken the foot. A direct comparison of the van der Waals and elastic energies shows that the van der Waals interaction remains a perturbation provided that $A_{gel} < S^3/G^2$. A rough estimate of the right hand side is given by $k_BT\xi_p^6/b^6$ (c^*-gel) which is indeed large compared to normal Hamaker constants.

In the next section we turn now to a more detailed description of the case of macroscopic gels. However, we shall see that the main physical ideas are already settled and, indeed, the most important quantity is the characteristic length ℓ.

Spreading of a Macroscopic Gel: $R > L$

Macroscopic Model

We consider first a macroscopic gel that adsorbs on a surface. To provide a reliable model we make use of classical elasticity theory.[8] For simplicity, we start from a gel with the shape of an infinite half cylinder of length L (see Figure 1), which enables the elastic problem to be considered in effect in two dimensions. The deformation properties involve just the elastic half-disk. The results do not depend on the length L.

The free energy for this reduced problem is given by the same general form as indicated in the introduction

$$F_{\mathrm{red}} = F_{\mathrm{el}} - S\,L \qquad (4)$$

where $L=2X$ is the length of the gel at the surface. The equilibrium is found by minimization

$$\frac{\partial F_{\mathrm{el}}}{\partial X} = 2S \qquad (5)$$

It is easy to imagine that the spreading parameter S acts as a concentrated force on the gel, i.e., on the centre of the semicircle. This problem is now associated with a classical elasticity problem first formulated by Hertz long ago. Later, Muskhelishvili[8] developed an elegant method to solve effective 2-D elasticity problems in the complex plane. We use his solution for a disk subject to concentrated forces acting on the ends of a diameter.

The geometry given in Figure 1 naturally suggests studying the problem in polar coordinates, where θ is the angle from the centre. The displacements on the surface along the Cartesian directions and in terms of the polar angle θ are given by

$$u_x = \ell\left(\log(\cot(\theta/2)) - \cos\theta\right) \qquad (6)$$

$$u_y = \ell\left(\frac{\pi}{2}\frac{1/2-\sigma}{1-\sigma} - \sin\theta\right) \qquad (7)$$

where we have redefined the elastic length $\ell = \frac{4S}{\pi G}(1-\sigma)$. Strictly speaking, on the diameter of action of the concentrated forces, the transverse displacement vanishes by symmetry (as can also be seen from the full solution in the complex plane). Formally, only when the application points are approached along the boundary, is a finite transverse displacement obtained. The macroscopic description can apply only down to some cut-off scale, in our case the mesh size of the gel (see below). The results deserve some physical discussion. The first observation is that the length scale for the deformation is ℓ. The extension parallel to the surface is singular, since the logarithmic term diverges for small values of θ. Physically this means that the macroscopic approach is no longer valid for angles $\theta < \theta_c \approx r_c/R$, where r_c is a lower cut-off of the order of the mesh size ξ_p of the network. The extension due to adsorption is then given by

$$u_x(\theta_c) = \ell\left(\log\cot\left(R/2\xi_p\right) - 1\right) \tag{8}$$

The reduction in the maximum height is given by

$$\Delta h = u_y(\pi/2) = \ell\left(\frac{\pi}{2}\frac{1/2-\sigma}{1-\sigma} - 1\right) \tag{9}$$

The equations show the significance of the special case $\sigma = 1/2$ which corresponds to (macroscopic) incompressible dry rubbers where the volume is not changed upon deformation. Note that all the lengths are of the order of the elastic length ℓ. The macroscopic contact angle defined at the inflexion point of the deformed gel profile is given by $\tan\psi = \frac{1}{2}\left(\left(R/\ell\right)^{1/2} - \left(R/\ell\right)^{-1/2}\right)$ in agreement with our previous estimate.

Let us briefly remark the specific results of dry rubbers under the condition $\sigma = 1/2$, since we may discuss the peculiarities of the logarithmic singularity in the lateral extension.

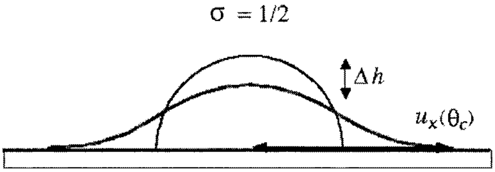

Fig. 2. The specific case of dry rubbers $\sigma = 1/2$ is special. All scales are indeed determined by ℓ in its original form.

First, the height of the gel always becomes smaller. The reduction of the height is written as

$$\Delta h = u_y(\pi/2) = \tilde{\ell} \tag{10}$$

The lateral extension as above is singular, i.e., $u_x \to \infty$, as shown already in the general result eq.(8). There is, however, a natural cut-off scale in the theory. Of course, at large values of u_x

the foot becomes thinner and thinner. The macroscopic theory can provide sensible results only as long as the foot thickness does not become smaller than the mesh size ξ of the gel, as depicted in Figure 3. This limit is also addressed to a cut-off of the angle θ in the form

$$u_x(\theta_c) = \tilde{\ell}\left(\log\cot(R/2\xi) - 1\right) \qquad (11)$$

This natural cut-off then determines the limiting size in the outer part of the foot to $r_c = \mathcal{O}(\xi)$, which corresponds to the value of the angle $\theta_c \approx r_c/R$.

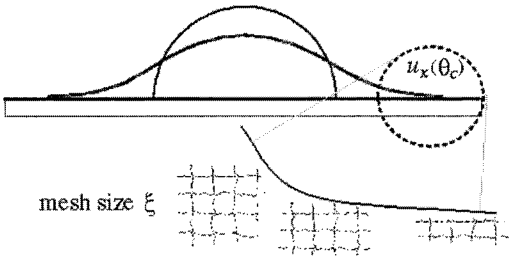

Fig. 3. The natural cut-off is determined by the mesh size (cross-link density) of the rubber. If the outer part of the foot is of the same size as the mesh size ξ, the validity of the theory breaks down (see the "enlarged" part of the foot).

Compressed Brushes and Adsorbed c^*-Gels: Mesoscopic Model

The cut-off angle motivates immediately an alternative way to consider the problem of gels near surfaces, which starts from a molecular description. The problem becomes very simple if we consider a so-called c^* gel, where the size of the mesh is given by its natural excluded volume scaling. When the gel adsorbs it spreads on the adsorbing surface at the edges to form a foot of size ℓ (see Figure 4). In the foot region, the chains stretch and tilt to become parallel to the surface. Furthermore, if we assume local affine deformations, the size of the chains increases by a factor of order unity and the stretching elastic energy per chain is of order k_BT. The number of chains involved per unit length is ℓ^2/ξ_p^3 and the elastic energy per unit length of the gel is

$$F_{el} \sim k_B T \ell^2/\xi^3 \qquad (12)$$

At mechanical equilibrium, this is of the order of the energy gain due to adsorption $S\ell$. Therefore we recover the value of the elastic length in the form

$$\ell \approx S\xi^3/k_BT \qquad (13)$$

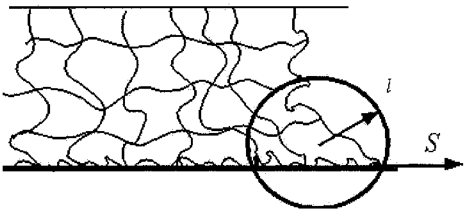

Fig. 4. The confinement and adsorption behaviour of c^*-gels. The geometry uses the ideas from above. The deformed region in the circle of radius ℓ determines a microscopic expression for the local deformation in the foot. The only length scale present is the mesh size, indicated by the (symbolic) lattice.

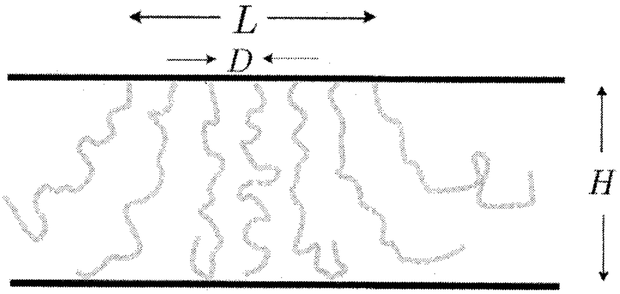

Fig. 5. The confinement of finite brushes shows similar behaviour. The confinement of the brush yields a similar foot at the edges of the brush. Its size is determined by the average distance between two chains (grafting density), the natural brush height and the height of the confinement.

It is interesting to note that this problem has strong relations with the confinement of finite polymer brushes on surfaces. This is illustrated in Figure 5.

Indeed the physics of gel adsorption shares several similarities with that of a polymer brush of finite size.[7] In a semi-infinite brush of grafting density $1/\xi^2$, all the chains within one brush thickness $h_0 \approx N/\xi^{2/3}$ from the edge present an overspill of about h_0 and form a foot. When the brush is compressed (Figure 6) to the height $h < h_0$, the edge effect penetrates over a much larger size $\ell^2 \sim h_0^3/h$. This penetration length can be found from a scaling argument.

We first assume that there is only one characteristic length scale ℓ in the grafting plane direction. The chains within a distance ℓ from the edge bend and form a "horizontal brush" (see Figure 6) parallel to the grafting surface (Fig. 2b). The number of chains per unit length perpendicular to the figure involved is ℓ/ξ^2 and the effective grafting density of the horizontal brush is $\sigma \sim \ell/(\xi^2 h)$. The "height" of the "horizontal brush" is given by the classical formula for the thickness of polymer brushes,[9] $\ell_{\mathrm{brush}} \approx N\ \sigma^{1/3}$. This has to be of the order of ℓ. Use of the well known values for scaling theories for polymer brushes yields immediately $\ell_{\mathrm{brush}} \approx \ell$, which is the announced value of ℓ.

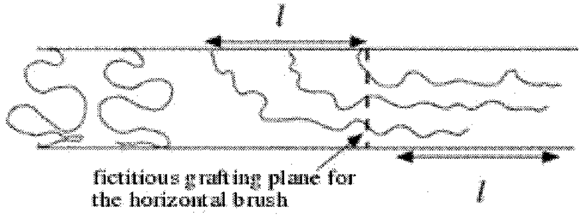

Fig. 6. The view of the confined brush at large confinement. The overspill can be seen as a horizontal brush with a fictitious grafting density at an imaginary grafting plane. Then the overspill is also determined by ℓ.

The problem can be treated in more detail, which is briefly illustrated here. To do so we divide the brush into slices (see Figure 7). The grafting density $\sigma \approx \frac{1}{D^2}$ is then mapped into the corresponding value for σ, which is determined by the number of chains in one slice. The elastic free energy in a slice though the brush can be written simply as

$$F_{\mathrm{el}} = \sigma k_{\mathrm{B}} T l \int_0^L dx \frac{\left(z(x)-x\right)^2 + H^2}{Na^2} \tag{14}$$

and the excluded volume free energy as

$$\mathrm{U} = l\,\upsilon\,\frac{N^2\sigma^2}{H}\int_0^L dx \frac{1}{1+\frac{dz}{dx}} \tag{15}$$

The free energy, i.e., the sum of both term can be minimized with respect to the profile $z(x)$, which will lead to corresponding differential equations. These can be solved exactly.[7]

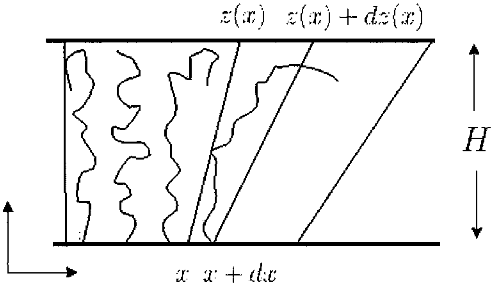

Fig. 7. The confinement of finite brushes shows a similar behaviour. The confinement of the brush yields a similar foot at the edges of the brush. Its size is determined by the average distance between two chains (grafting density), the natural brush height and the height of the confinement.

Here we do not give the exact solution, since it will be sufficient to mention the approximation for small overspills. The profile is given by

$$z(x) = x + h_0 \left(\frac{h_0}{H} \right)^{1/2} \exp\left\{ \frac{x}{h_0} \left(\frac{H}{h_0} \right)^{1/2} \right\} \qquad (16)$$

where the correlation length

$$\ell = h_0 \left(\frac{h_0}{H} \right)^{1/2} \qquad (17)$$

agrees with that given before by simple scaling. However, it is interesting to note that this result is consistent with the Skoulius length for the equilibrium situation $h = H$.[7]

Spreading of Microgels: $\ell > R$

Small pieces of gel that can be characterized by the condition $R < \ell$ are microgels. These flatten on the interface upon adsorption and in that sense it strongly adsorbs. At the scaling level, when the gel is highly stretched, the physical behaviour is dominated by the elastic properties of the individual chains. We consider here microgels with a size R, between ℓ and the mesh size ξ_p, which has been determined already earlier as the natural lower cut-off size. We use the affine deformation model for gel elasticity, which allows to account for the dependence of the elastic moduli on the preparation state of the gel. The affine deformation model might seem crude when applied to microgels. The elastic length ℓ being irrelevant for microgels ($R < \ell$), the only remaining scale (larger than the mesh size) is the sample size. We thus expect that the affine deformation model holds at the scaling level.

Equilibrium Solvent Spreading

So far we discussed dry gels only. In the context of wet gels at initially dry interfaces, we have an additional interplay between the solvent molecules and the surface. There are situations where the solvent can leak from the gel and spread on the surface forming a thin film around the gel. We will consider here the case of a piece of gel in the macroscopic regime ($R > \ell$) and a perfectly wetting solvent. On the one hand the solvent wants to spread over the surface, on the other hand the solvent swells the gel and the gel and the surface compete for the solvent. Experiments in this context have been proposed already[12-14] and are described in an early model.[15] The description of a macroscopic piece of gel is dominated by the bulk contribution to the free energy. A suitable free energy for the gel of volume υ_{gel} and volume fraction $\phi = cb^3$ is given by

$$\frac{F_{gel}}{\upsilon_{gel}} = \frac{k_B T}{b^3}\left(\phi^{9/4} + \frac{\phi}{N}\left(\frac{\xi}{bN^{3/5}}\right)^{5/2}\right) \tag{18}$$

The first term describes the swelling pressure, whereas the second term represents the elastic free energy per unit volume of the stretched elastic chains. ξ is the mesh size in the swollen state and υ_{gel} the total gel volume. We assume here that the elastic chains are stretched beyond their isolated excluded volume size N^{ν}, as is the case at swelling equilibrium in a solvent bath.

The volume υ_{gel} of the gel can be expressed as the ratio of the polymer volume and the volume fraction of the solvent ϕ, $\upsilon_{gel} = \upsilon_{pol}/\phi$. As above, we use a simple affine model for the deformation under swelling. The mesh size is $\xi = \xi_p \mu^{-1/3}$. The volume fraction ϕ is related to the (inverse) deformation ratio and the volume fraction in the preparation state by $\phi = \phi_p \mu$. Inserting these relations into the free energy we find for the equilibrium deformation (swelling) in excess solvent

$$\mu_{\mathrm{eq}} = \frac{\xi_{\mathrm{p}}^{6/5}\phi_{\mathrm{p}}^{-3/5}}{b^{6/5}N^{6/5}} \tag{19}$$

We introduce the overlap in the preparation state $\alpha = c_{\mathrm{p}}\ \xi_{\mathrm{p}}^{3}/N$, which is equal to one if the gel has been prepared at the overlap concentration c^* and to $N^{1/2}$ if the gel has been prepared in the melt. The swollen mesh size $\xi \sim \alpha^{1/5}N^{3/5}b$ is indeed larger than the Flory radius (the c^*-gel being marginal). The equilibrium gel concentration $\phi_{\mathrm{eq}} \sim \alpha^{2/5} N^{-4/5}$ is larger than the overlap concentration except for a c^*-gel.

Let us consider the solvent film on the surface, which has a thickness h_υ and covers a certain area. The wetting behaviour can be described by the balance between the long range van der Waals interactions and the capillary forces. The van der Waals free energy per unit area is written as $P(h)=A/h_\upsilon^2$ where the Hamaker constant A is of the order of $10k_{\mathrm{B}}T$. The free energy of a film of volume υ_{film} is written as

$$F = -\frac{S_s\upsilon_{\mathrm{film}}}{h_\upsilon} + \frac{A}{h_\upsilon^2}\frac{\upsilon_{\mathrm{film}}}{h_\upsilon} \tag{20}$$

Here $S_s > 0$ is the spreading parameter of the solvent on the surface. The minimization of this free energy yields the equilibrium film thickness. We assume for simplicity that the van der Waals film spreads freely, if the film area is imposed by the substrate, the film thickness departs from its unconstrained optimum $h_\upsilon \approx (A/S_s)^{1/2}$.

The mixed problem, i.e., gel in presence of a solvent film can be described correspondingly by using these two free energies in a simple way. If the gel is not in contact with the surface, its (inverse) deformation factor is μ_{i}. On the surface, some of the solvent leaks out of the gel and the gel deswells; its (inverse) deformation μ is larger. The corresponding free energy is given by

$$F = k_{\mathrm{B}}T\frac{\upsilon_{\mathrm{pol}}}{b^3}\left(\mu^{5/4}\phi_{\mathrm{p}}^{5/4} + \frac{\mu^{-5/6}}{N}\left(\frac{\xi_{\mathrm{p}}}{bN^{3/5}}\right)^{5/2}\right) + \upsilon_{\mathrm{film}}\left(\frac{A}{h_\upsilon^3} - \frac{S_s}{h_\upsilon}\right) \tag{21}$$

The parameters A and S_s determine the equilibrium shape of the system. The solvent is sucked out from the gel and wets the surface if the spreading S_s is large enough. The volumes of the film and of the gel are related by the mass balance

$$\upsilon_{\mathrm{film}} = \frac{\upsilon_{\mathrm{pol}}}{\phi_{\mathrm{p}}}\left(\frac{1}{\mu_i} - \frac{1}{\mu}\right) \tag{22}$$

The free energy can then be written as a function of the deformation μ.

$$F_{\text{film+gel}} = \upsilon_{\text{pol}} \left\{ \frac{k_{\text{B}}T}{b^3} \mu^{5/4} \phi_{\text{p}}^{5/4} + \frac{k_{\text{B}}T}{Nb^3} \left(\frac{\xi_{\text{p}}}{bN^{3/5}} \right)^{5/2} \mu^{-5/6} - \left(\frac{1}{\mu_i} - \frac{1}{\mu} \right) \frac{1}{\phi_{\text{p}}} \left(\frac{4S_s^3}{27A} \right)^{1/2} \right\} \qquad (23)$$

In the last part of the above equation the optimized film free energy per unit volume $F_{\text{film}} = -(4S_s^3/27A)^{1/2}$ has been inserted. At the optimum the film disjoining pressure is balanced by the gel osmotic pressure. Only gels for which the initial deformation μ_{i} is smaller than the final deformation μ can lose some solvent.

If $S_sb^3/h>\phi_{\text{eq}}^{9/4}$, where $\phi_{\text{eq}} = \mu_{\text{eq}}\phi_{\text{p}}$ is the gel concentration at maximum swelling calculated previously, the gel is severely starved of solvent in the final state (where the osmotic pressure is dominated by the interaction term) and

$$\mu \approx \left(\frac{S_sb^3}{h_\upsilon} \right)^{4/9} \frac{1}{\phi_{\text{p}}} \qquad (24)$$

The final gel concentration is then fixed by the film parameters $\phi_{\text{f}} \approx (S_sb^3/h_\upsilon)^{4/9}$. For large values of S_s, $S_s > h_\upsilon/b^3$, almost all the solvent is sucked out. In the opposite case ($S_sb^3/h_\upsilon < \phi_{\text{eq}}^{9/4}$), the gel stays close to its maximum swelling characterized by the concentration ϕ_{eq}. Both contributions to the osmotic pressure are important and

$$\frac{\delta\phi}{\phi_{\text{eq}}} \approx \phi_{\text{eq}}^{9/4} \frac{S_sb^3}{h_\upsilon} \qquad (25)$$

with $\delta\phi=\phi_{\text{f}}-\phi_{\text{eq}}$. In principle one could also consider the reverse process where an initially dry gel sucks solvent from a wet surface. The analysis may then be complicated by dynamic processes such as film rupture as opposed to gentle film retraction.

Final Remarks

We have considered gels at adsorbing surfaces. In contrast to ordinary liquids that may spread freely, the spreading of gels is limited by the elastic forces which develop upon deformation. The shear modulus G and the gain in surface tension upon gel adsorption S entail an elastic length $\ell \sim S/G$. Macroscopic gels with a size larger than ℓ deform only at the edges over a length ℓ due to the elastic stresses transmitted by the cross-links. Microgels with a size smaller than ℓ

display finite deformations despite the existence of cross-links.

Although the gel cannot spread freely, the (good) solvent which swells the gel can. We consider a wet gel on a dry substrate. If the solvent wets the substrate it may be (at least partially) sucked out of the gel. This happens if the osmotic pressure in the gel is lower than the disjoining pressure in the a solvent film around the gel. Unless the two pressures are very close, the final gel is very starved of solvent and its concentration is imposed by the film.

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