Deformation-Induced Anomalous Swelling of Topologically Disordered Gels

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ABSTRACT: We discuss the scaling theory of topologically disordered swollen networks and apply it to the study of uniaxially and biaxially stretched gels. While in Θ-solvents the response to deformation is qualitatively similar to that of usual elastic solids, the theory predicts that under good solvent conditions there exists a range of intermediate deformations for which the gel swells normal to the stretching direction and its elongational modulus is reduced. At larger deformations there is a crossover into a new regime in which the gel is stabilized by nonlinear restoring forces. The experimental ramifications of our results are discussed.

1. Introduction

The present understanding of elastic and swelling phenomena in gels is based on the notion that both the equilibrium state of gel and its response to external perturbations are determined by the interplay between elastic (solid-like) and osmotic (liquid-like) effects.[1,2] According to the strong additivity assumption of Flory and Rehner,[2] the elastic contribution to the free energy arises as the result of the reduction of conformational entropy produced by the stretching of network chains and is the same in a swollen gel and in a dry network (provided that the effective spring constant is corrected for the swelling of chains in a good solvent). The osmotic contribution is identical to the free energy of un-cross-linked chains (under the same solvent conditions) and can be evaluated using Flory–Huggins mean-field theory.

Although the classical theory of gels proved to be quite successful, both comparison with experiment and fundamental considerations led to a number of modifications of the original models. Most of the revisions maintain the strong additivity assumption and attempt to give an improved description of the elastic or of the osmotic terms *separately*. Thus, following the success of scaling theories of semidilute polymer solutions,[3] the mean-field description of the liquid-like contribution to the free energy of a swollen gel was replaced by a scaling one.[4] In other works, the simplest Flory-type treatment of the elastic part of the free energy was modified to incorporate certain features of real gels.[5] More recently, the strong additivity assumption itself was questioned. It was argued that experimental observations (e.g., differential swelling experiments[6]) support the introduction of a weaker form of this assumption, which maintains the partition of the free energy into solid-like and liquid-like contributions, but the later is no longer equal to the free energy of the corresponding solution.[7]

At first glance it seems that the weak additivity assumption allows one to choose the proper models for the description of solid and liquid parts *independently*. However, experience with Flory-type mean-field arguments suggests that such a procedure is not self-consistent and that an improved description of only one of the contributions to the free energy may lead to erroneous results.[3] One can therefore argue on purely theoretical grounds that the application of scaling theory to the description of the liquid-like part of the free energy of the gel *dictates* a corresponding modification of the elastic term. Such modification was recently proposed by Panyukov[8] and by Obukhov et al.,[9] who analyzed the equilibrium swelling and the concentration dependence of the moduli in the scaling regime and discussed the experimental evidence in support of their predictions.

In this work we consider topologically disordered gels for which a self-consistent scaling description is expected to be valid and derive the general relations between the exponents which determine the concentration dependence of osmotic and elastic moduli in a Flory-type scaling theory of gel elasticity. We analyze the deformation of the gel (uniaxial and biaxial) under various solvent conditions and show that, under good solvent conditions, there exists a range of finite elongations for which a gel can minimize its elastic and osmotic free energies by swelling in directions perpendicular to the axis of stretching (i.e., has a negative effective Poisson ratio). We derive the force–elongation relations and find that, in the above regime, the gel "softens"; i.e., its effective elongational modulus decreases. At yet higher elongation there is a transition to a Pincus-like nonlinear regime of gel elasticity previously discussed by one of the present authors,[10] and in this range the gel exhibits a positive effective Poisson ratio. In conclusion we discuss the limitations of this work and propose experiments which can test our predictions.

2. Scaling Theory of Topologically Disordered Gels

The simplest model of swelling equilibrium of polymer gels in good solvents is the so-called "c^* theorem"[3] according to which the network expands in excess solvent until it reaches a state which resembles a solution of chains at the overlap concentration c^*. In this model, the assembly of cross-linked chains can be replaced by a space-filling regular lattice of spheres, such that *only spheres which occupy nearest neighboring lattice sites are connected by chains of length N*. While the above picture is appealing in its simplicity, real gels have, as a rule, more complicated topological structure. Even if one sets aside the issue of cross-link density inhomogeneities, one needs to take into account the nonphantom nature of real chains (chains cannot cross each other). Since in the melt there are of order $N^{1/2}$ chains in the volume spanned by a chain of N monomers, one expects that when a gel is formed in the melt or in a concentrated solution and then diluted in excess solvent, these chains cannot disentangle in the process of swelling and there remain many chains in the volume spanned by a single chain.[11] This leads to a disordered topological structure of the gel (Figure 1) in which *cross-link points which are neighboring in space*

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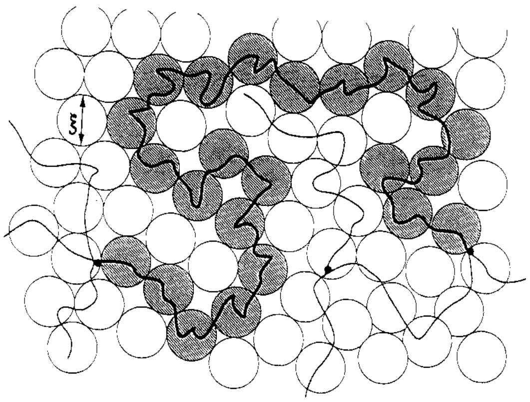

Figure 1. Schematic representation of a topologically disordered gel. The blob size is ξ.

are not, in general, topological neighbors (i.e., connected by a network strand of length N). If entanglement contributions to the elastic moduli can be neglected (i.e., if entanglements do not act as effective cross-links), it can be shown that the elasticity of this topologically disordered network can be described by the usual Flory mean-field theory of gel elasticity, provided that one uses blobs of size ξ rather than statistical segments as basic elements of polymer molecules[8] (see Figure 1). These concentration blobs play exactly the same role as in the scaling description of semidilute polymer solutions, i.e., intrachain excluded-volume correlations are maintained within the blobs and screened on length scales larger than the blob size. Within the affine approximation, the elastic contribution to the free energy of the swollen network is identified with the entropic penalty for deforming an ideal chain of *blobs*. The elastic part of free energy in this rescaled Flory-like description of an affine network is given by (in units of k_BT)

$$F_{el}^{scal} \simeq \sum_{chains} \frac{R^2}{N_b \xi^2} \simeq \frac{g(\xi)}{\xi^2} \sum_{chains} \frac{R^2}{N} \simeq l^2 \frac{g(\xi)}{\xi^2} F_{el}^{dry} \qquad (1)$$

where F_{el}^{dry} and F_{el}^{scal} are the dry network and the scaling expressions for the elastic free energies, l is the statistical segments length, ξ is the blob size, N_b and $g(\xi)$ are the numbers of blobs per chain and monomers per blob, respectively, and the summation is over all elastically active chains. The blob size ξ scales with a power of concentration with an exponent which depends on the quality of solvent:[3]

$$\xi \propto \begin{cases} c^{-3/4} & \text{in a good solvent} \\ c^{-1} & \text{in a }\Theta\text{-solvent} \end{cases} \qquad (2)$$

The total osmotic (swelling) pressure can be written as $\Pi_{osm} = \Pi_{liq} - \Pi_{net}$ where the liquid-like contribution to the osmotic pressure is[3]

$$\Pi_{liq} \simeq \frac{k_BT}{\xi^3} \qquad (3)$$

The elastic network contribution to the total osmotic pressure can be obtained from F_{el}^{scal}:

$$\Pi_{net} = \frac{\partial F_{el}}{\partial V} \propto c^{4/3}\xi(c) \qquad (4)$$

Π_{net} represents the effect of elastic restoring forces which tend to compress the swollen network. Within Flory-type theories $\Pi_{net} \simeq \mu$, where μ is the shear modulus of the gel. From eqs 1–4 one can easily find that the condition that Π_{liq} and Π_{net} scale as powers of concentration, $\Pi_{liq} \propto c^m$ and $\Pi_{net} \simeq \mu \propto c^n$, imposes the following relationship between the exponents n and m:

$$n = \frac{4-m}{3} \qquad (5)$$

In the particular cases of Θ and good solvent regimes for the network, one recovers the known values of the exponents m and n: (a) In the Θ region where the second virial coefficient vanishes and the liquid-like contribution to the osmotic pressure scales as $\Pi_{liq} \propto c^3$, we obtain the classical result for the concentration dependence of the shear modulus,[1] $\mu \propto c^{1/3}$. (b) In the good solvent regime where $\Pi_{liq} \propto c^{9/4}$, we recover the recent result of Obukhov et al.[9], $\mu \propto c^{7/12}$. Although there is some experimental evidence in support of the latter scaling law in good solvents,[12] other experiments[4] indicate that the shear modulus scales with a 1/3 power of concentration, independent of quality of solvent, a result inconsistent with our hyperscaling relation, eq 5. A possible reason for the above discrepancy is the existence of monomer and cross-link density inhomogeneities in the gel, which arise due to the random character of the process of cross-linking. Such inhomogeneities were not taken into account in the derivation of (5) where it was assumed that elastically active chains experience the same solvent conditions throughout the gel and, therefore, our simple scaling considerations do not apply to gels in which large cross-link density fluctuations exist. One can imagine a situation in which elastically active chains embedded in the denser regions experience worse solvent conditions (due to higher local concentration of cross-links which may reduce the effective local solubility of the network) than those in the more dilute regions. If the dense regions percolate through the gel, one may expect that while the shear modulus is controlled by the denser regions and therefore scales with a classical (1/3) exponent, the liquid-like contribution to the total osmotic pressure is dominated by the strongly swollen regions and, due to better local solvent conditions, scales as $c^{9/4}$.

3. Deformation of Swollen Gels

One can use eqs 1–3 to write the general form of the Flory–Rehner-type scaling free energy for an arbitrary deformation of the gel:

$$F = A(\lambda_0^3 Q)^a \lambda_0^2(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) + B(\lambda_0^3 Q)^b \qquad (6)$$

where $\lambda_0 = (V_0/V_{prep})^{1/3}$ is the equilibrium swelling ratio and V_{prep} and V_0 are the volumes of gel under preparation conditions and in the swollen state before the deformation, respectively. Here and in the following we consider only the case $V_{prep} \leq V_0$; otherwise one has to use the modified form of free energy of ref 9. Defining $\alpha_i = \lambda_i/\lambda_0$, where λ_i is the deformation ratio along the ith direction ($i = x,y,z$ are the principal axes of deformation), $Q = \alpha_x\alpha_y\alpha_z$ represents the change of the gel volume as a result of deformation. Note that all dependence on the state of preparation cancels out in the definitions of α_i and of Q and that the deformation is defined with respect to the equilibrium swelling state. The exponents a and b can be easily determined from eqs 1–3: $a = -1/4$, $b = -5/4$ for a good solvent, and $a = 0$ (no rescaling), $b = -2$ for Θ-solvent conditions. In general, the constants A and B depend on the particular gel–solvent combination, gel preparation and temperature.

Uniaxial Deformation. Consider the uniaxial deformation of a gel under various solvent conditions. In studies

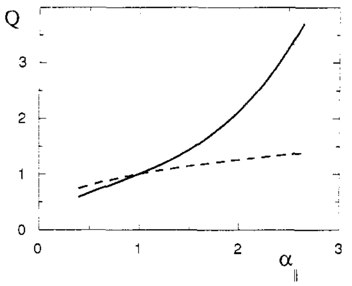

Figure 2. Dependence of the volume expansion factor Q on the elongation ratio $\alpha_\parallel$. The solid and dashed lines correspond to good and Θ-solvent cases, respectively.

of transient response to deformation one typically observes the gel on time scales which are long enough for stress relaxation to take place but which are much shorter than the time needed for the solvent to flow out of or into the gel (this time is determined by cooperative diffusion through the gel sample and can be of the order of hours or days). In this type of experiments the deformation is volume-preserving and the gel is in mechanical rather than in thermal equilibrium. In the present work we are interested in the steady-state response to deformation in the presence of excess solvent, in which case the transverse dimensions of a gel are determined by minimizing its free energy with respect to the volume, at a fixed imposed deformation. Note that while in the former case one measures the *bulk* moduli, in the latter case one obtains the *osmotic* elastic constants of the gel. The free energy (eq 6) associated with uniaxial deformation can be written as

$$F = A(\lambda_0^3 Q)^a \lambda_0^2(\alpha_\parallel^2 + 2Q\alpha_\parallel^{-1}) + B(\lambda_0^3 Q)^b \qquad (7)$$

where the ratio of the coefficients A and B determines the equilibrium swelling ratio (λ_0) in excess solvent. The connection between the steady-state volume of the gel and the given deformation ($\alpha_\parallel$) along the stretching direction is given by the minimization condition:

$$\left.\frac{\partial F}{\partial Q}\right|_{\alpha_\parallel} = 0 \qquad (8)$$

The substitution of eq 7 in eq 8 gives the following equation for Q:

$$(3a + 2)Q^{b-a-1} = a\alpha_\parallel^2 Q^{-1} + 2(a + 1)\alpha_\parallel^{-1} \qquad (9)$$

The dependence of Q on $\alpha_\parallel$ for different solvent conditions is plotted in Figure 2. As expected from the concentration dependence of the osmotic contribution to the free energy (eq 7), the volume of the gel increases with the deformation and, since repulsive interactions are stronger in good solvents than in Θ-solvents, this increase is smaller in the latter case. The qualitative difference between the two cases becomes apparent when one expresses the steady-state transverse dimensions of the gel ($\alpha_\perp$) as a function of the imposed deformation ($\alpha_\parallel$). Substituting $Q = \alpha_\parallel\alpha_\perp^2$ into eq 9, we obtain

$$\alpha_\perp^2 = \frac{\alpha_\parallel^2}{12}\left(1 + \left(1 + \frac{120}{\alpha_\parallel^5}\right)^{1/2}\right) \qquad (10a)$$

in the good-solvent case and

$$\alpha_\perp = \alpha_\parallel^{-1/3} \qquad (11a)$$

in the Θ-solvent case. Inspection of eq 11a shows that, in Θ-solvents, the lateral size of the gel is a monotonically decreasing function of elongation (Figure 3). Under good-solvent conditions, eq 10a predicts that, *for sufficiently small deformations*, $\alpha_\perp$ is the decreasing function of elongation ratio $\alpha_\parallel$ but that this decrease (i.e., the Poisson ratio σ) is much smaller for good ($\sigma = 3/22$ when $\alpha_\parallel \to 1$) than for Θ ($\sigma = 1/3$) solvents. Notice that both values are smaller than the 0.5 Poisson ratio for incompressible solids, a value which is usually used in the analysis of stress–strain relations in gels. The latter value strictly applies only to transient experiments in which the gel is observed on time scales shorter than the relaxation to the steady-state configuration and therefore is deformed at constant volume.

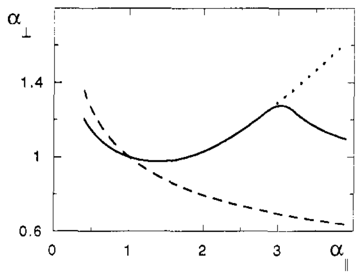

Figure 3. Deformation ratio in the perpendicular direction, $\alpha_\perp$, as a function of the elongation ratio, $\alpha_\parallel$. The solid and dashed lines correspond to good and Θ-solvent cases, respectively. The crossover from Flory (eq 10a) to Pincus behavior (eq 14) takes place at $\alpha_\parallel \approx 3$; the continuation of the Flory branch into the high-elongation regime is given by the dotted curve.

The predicted decrease of the Poisson ratio with increasing solvent quality has been observed experimentally but the reported values of this ratio in good solvents are usually higher[13] than 3/22 (unfortunately, since the concentration dependence of the shear modulus was not reported by the authors, we do not know whether the discrepancy is related to the difference between the predicted 7/12 and the observed 1/3 exponents for the shear modulus). A recent experiment[14] on NIPA gels which undergo a volume phase transition has reported a change of Poisson ratio from 0.15 to 0.3–0.4 as the quality of solvent was changed from good to Θ conditions by increasing the temperature at high ionic strength, in excellent agreement with our predictions.

A closer look at eq 10a shows that, in the good-solvent case, there exists a regime of *finite magnitude deformations* (corresponding to strains of order unity) in which $\alpha_\perp$ *increases* with increasing $\alpha_\parallel$ (Figure 3). If one defines a deformation-dependent effective Poisson ratio through $\sigma_{\mathrm{eff}} = (1 - \alpha_\perp)/(\alpha_\parallel - 1)$ (notice that this reduces to the usual definition of the Poisson ratio in the limit of infinitesimally small deformations), this ratio becomes negative in the above regime. The origin of this extraordinary behavior is the unusual concentration dependence of the elastic free energy of a gel in a good solvent in our model. Notice that the osmotic contribution to the free energy decreases monotonically with Q and therefore always favors expansion of the gel. At small uniaxial deformations the swelling is moderated by the $Q\alpha_\parallel^{-1}$ contribution to the elastic free energy, which increases with Q and thus suppresses swelling. At larger extensions this contribution becomes negligible with respect to the $\alpha_\parallel^2$ term which has an effective spring constant that decreases with dilution in a good solvent (as $Q^{-1/4}$). In this range, both osmotic and elastic terms favor swelling of the gel, and the resulting dramatic expansion (Figure 2) gives rise to a negative effective Poisson ratio.

We now consider the force–elongation relations for uniaxially deformed gels. Defining the force needed to

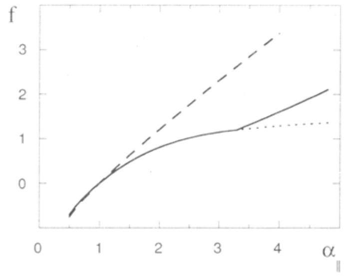

Figure 4. Plot of the force f (in units of $2A\lambda_0^{3a+2}/L_0$) as a function of the elongation ratio $\alpha_\parallel$ for good solvent (solid line) and Θ-solvent (dashed line). The crossover from Flory (eq 12) to Pincus behavior (eq 13) takes place at $\alpha_\parallel \approx 3$; the continuation of the Flory branch into the high-elongation regime is given by the dotted curve.

hold the gel at elongation $\alpha_\parallel$ as $f = L_0^{-1}\,\mathrm{d}F/\mathrm{d}\alpha_\parallel$, where L_0 is the equilibrium length of the swollen gel, we can express this force as a function of the deformation ratio:

$$f_{\mathrm{Flory}} = 2\frac{A}{L_0}(\lambda_0^3 Q)^a \lambda_0^2(\alpha_\parallel - \alpha_\perp) \tag{12}$$

The force–elongation curves are plotted in Figure 4, for both Θ and good solvents. For good solvents we observe that in the regime corresponding to a negative effective Poisson ratio, the slope of the force–elongation curve decreases with elongation; i.e., the effective elongational modulus "softens". This effect is produced by the combination of elongation-induced swelling of the gel (see Figure 2) and the weakening of the effective spring constant upon dilution, which results from our model for the elastic free energy, eq 7.

At yet larger elongations, the deformation can no longer be described by Flory-like pseudolinear elasticity (eq 7) and a *new nonlinear force–elongation law must be introduced.*[10] Neglecting small corrections due to the osmotic contribution to the free energy, we obtain

$$f_{\mathrm{Pincus}} \propto \alpha_\parallel^{3/2} \tag{13}$$

The onset of the strong deformation regime corresponds to a state in which the Gaussian chains of blobs become fully stretched and further deformation proceeds through the Pincus mechanism.[15] In this regime stretching of the chains leads to screening of intrachain excluded-volume correlations and increases the number of "tensile" blobs while decreasing their size. This affects the osmotic pressure and may lead to swelling or deswelling of the gel. A simple calculation[10] shows that the net effect is to produce a weak decrease of the transverse dimensions of the gel upon stretching,

$$\alpha_\perp \propto (\alpha_\parallel)^{-1/4} \tag{14}$$

i.e., a positive effective Poisson ratio is recovered (see Figure 3). A straightforward estimate of the onset of this regime shows that it takes place at an elongation ratio $\alpha_\parallel^{\mathrm{onset}} \simeq dN^{1/5}$, where d is a constant of order unity.

In Figure 5 we present a schematic description of the steady-state behavior of a network swollen in a good solvent, at progressively increasing elongations. At small elongations, the Poisson ratio is positive and the transverse dimensions of the gel shrink with increasing applied strain (Figure 5b). At higher elongations this ratio becomes negative and the gel expands normal to the stretching axis (Figure 5c). Finally, for elongations larger than that corresponding to the crossover to Pincus regime, the effective Poisson ratio becomes positive again, and the transverse dimensions of the gel shrink upon further extension (Figure 5d).

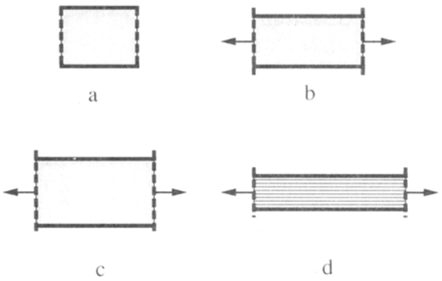

Figure 5. Schematic representation of gel deformation in a good solvent: (a) equilibrium state; (b) small elongation (Flory regime (positive Poisson ratio)); (c) intermediate elongation (Flory regime (negative Poisson ratio)); (d) large elongation (Pincus regime).

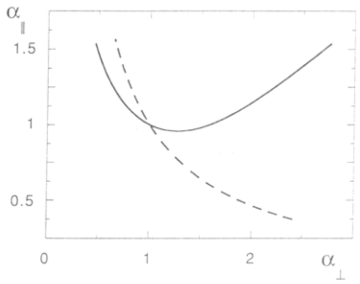

Figure 6. Deformation ratio in the parallel direction as a function of the transverse stretching ratio for biaxial deformations. The solid and dashed lines describe good and Θ-solvent cases, respectively.

Biaxial Deformation. One can find the connection between $\alpha_\parallel$ and $\alpha_\perp$ for biaxial deformation (now $\alpha_\perp$ is fixed and $\alpha_\parallel$ is varied to minimize the free energy, eq 6) in a good solvent, in a manner similar to that described in the discussion of uniaxial deformation:

$$\alpha_\perp^2 = \frac{7}{4}\alpha_\parallel^2\left(1 \pm \left(1 - \frac{40}{49\alpha_\parallel^5}\right)^{1/2}\right) \tag{10b}$$

In Θ-solvent

$$\alpha_\parallel = \alpha_\perp^{-1} \tag{11b}$$

The results are plotted in Figure 6. Notice that for sufficiently large biaxial extensions, the gel swells along the longitudinal direction. This regime of strain-induced swelling is qualitatively similar to the negative Poisson ratio regime predicted for the uniaxial case, though the effects are larger in the present case.

4. Discussion

We presented a scaling theory of osmotic and elastic effects in topologically disordered swollen gels. We found that in good solvents there exists a regime of intermediate elongations (strains of order unity) in which stretching produces swelling in the perpendicular directions and the resulting dilution leads to softening of the effective elongational modulus. At yet higher elongations we predict a crossover to a nonlinear regime in which the effective modulus increases with deformation and a positive effective Poisson ratio is recovered. Although our results were derived using the affinity assumption which is probably violated on microscopic length scales, we believe that the theory captures some of the essential physics of real polymer networks in good solvents and that the predicted trends should be observable.

A potential problem concerning the experimental realization of some of the predicted effects involves the conflicting requirements on the length of the chains between cross-links. Strictly speaking, the model applies only to the case of sufficiently short chains for which contributions to the shear modulus from effective cross-links formed by trapped entanglements can be neglected (actually, this condition is not too restrictive since the chain length should only be smaller than the entanglement length for a chain of *blobs*). On the other hand, the Pincus regime of chain deformation can only be observed for sufficiently long chains for which a significant range of elongations, $1 \ll \alpha_{\parallel} \ll N^{1/2}$, exists. A more delicate issue is the domain of applicability of the present scaling model of topologically disordered gels. The theory strictly applies only to gels made of chains of identical length N, e.g., made by end-linking a monodisperse melt or a concentrated solution. Random cross-linking in the melt produces an exponential distribution of chain lengths and gives rise to complex elastic behavior of individual network chains,[16] which may lead to the breakdown of our mean-field approach, eq 1.

We would like to stress that, following the discussion in section 2, it seems plausible to restrict the search for the predicted effects to those gel–good solvent combinations which exhibit the 7/12 scaling exponent of the shear modulus with concentration. Studies of the temperature dependence of the force–elongation relations are also of interest since, according to our model, all the predicted anomalies appear only in good solvents and should disappear as the Θ point is approached.

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