the behavior of the segmental motion in terms of the molecular shape and intermolecular interaction of the segments.

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Scattering by Deformed Swollen Gels: Butterfly Isointensity Patterns

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ABSTRACT: We discuss the case of gels prepared by statistical cross-linking of semidilute solutions. When swollen, such gels should show large-scale inhomogeneities related to the random distribution of tie points. We argue that, under uniaxial stretching, the concentration fluctuations spectra should exhibit an unusual anisotropy, which should be revealed by scattering experiments. We expect the scattering intensity in the direction parallel to the stretching to be stronger than in the perpendicular one.

I. Introduction

Properties of gels are strongly influenced by large-scale heterogeneities in the network structure.[1,2] In the swollen state these imperfections manifest themselves in a nonuniformity of polymer concentration. In practice the heterogeneities may arise for very different reasons. We have analyzed recently how in the case of cross-linking of a polymer solution, the random distribution of tie points may lead to important fluctuations in the local cross-linking density even when the reaction has been stopped far beyond the gel point.[3] These fluctuations, almost undetectable in the reaction bath, are revealed by swelling of the network. As a result the swollen gels should exhibit fractal heterogeneities in polymer concentration. Recent scattering experiments seem to confirm this picture.[4] The purpose of this article is to show the importance of the concentration heterogeneities to the properties of the uniaxially deformed gels. In particular we argue that even a very small uniaxial stretching should lead to an unusual scattering spectrum characterized by an increase of intensity in the direction parallel to the stretching and to isointensity curves of very unusual shape, known as "butterfly patterns".[5] Very recently, Onuki,[11]

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on the basis of classical elasticity theory has predicted anisotropic scattering ("normal" butterfly patterns) with a decrease of scattered intensity in the direction of stretching and an increase in the perpendicular direction. The point of this paper is to argue that heterogeneities inherent to the gel structure may, in some situations, inverse the direction of the anisotropy of the scattered spectra.

Such "abnormal" butterfly patterns have been observed in various systems, e.g., networks swollen by short labeled chains,[5,6] mixtures of short and long homopolymers[6,7] or copolymers and homopolymers,[8] and swollen smectics.[9] It should be stressed that although the spectra have similar features, the physical origin of the effect may be very different.[9-11]

II. Heterogeneities in Randomly Cross-Linked Networks

Very often gels are prepared by adding cross-linking agents to concentrated solutions of precursor long chains. For example, a considerable effort has been devoted recently to studies of the Friedel–Crafts reaction of polystyrene solutions with various cross-linking agents (e.g., dichloro-*p*-xylene[12] and dichloromethylanthracene[13]). When the precursor chains are very long ($M > 10^6$) and widely entangled (e.g., c = 5 to 20%), the gel point is reached very rapidly (a few minutes or even less). From this stage, the reaction proceeds in a more or less "frozen" semidilute solution. We focus on such a process, which we model as an instantaneous cross-linking of the initial semidilute solution.[3] Our picture is based on the assumption that the effective *interchain* tie points are statistically distributed among the interchain contact points that existed in the solution. We neglect correlations in the spatial distribution of the tie points and we suppose the lattice to remain unaffected by the cross-linking; i.e., we neglect the local elastic retraction of the network. We assume also that the solvent is a good solvent for the cross-linking agents, so there is no demixing effect in the reaction bath. Under these assumptions, the intensity scattered by the system essentially does not vary during the reaction process: random introduction of tie points does not modify the polymer concentration fluctuations on scales larger than the semidilute correlation length ξ_r.

Altogether, we describe the system as a random distribution of cross-links on a lattice formed by the interchain contact points in the solution. When two junctions are located on neighboring lattice sites, a "frozen blob" is formed. When swelling, it will be difficult to move these cross-links apart from each others, since they are connected by a chain segment that is already in an optimal excluded-volume conformation. Frozen blobs are often connected and form clusters of first topological neighbors.[14] Thus we describe the random cross-linking of chains as a site percolation on a blob lattice. The average size and the spread of size distribution of the clusters of frozen blobs increase when the percolation threshold is approached. For a true semidilute solution of long chains, many more cross-links must be introduced to reach this blob percolation threshold than to pass the gel point of the chains.[15] Thus, even well beyond the gel point when practically no unreacted chain could be extracted, strong inhomogeneities in cross-linking density can remain. Now when the gel is immersed in a good solvent it swells. We expect that the frozen blob clusters will expand less than the interstitial medium. The swelling process can be represented as a dilution of the clusters of frozen blobs accompanied by a partial expulsion of smaller clusters from the larger ones. Frozen blobs are no more distributed at random: the system looks like a solution of partially overlapping strongly polydisperse clusters in a less concentrated interstitial medium (Figure 2). Hence, large-scale spatial fluctuations of monomer concentration are present in a range characterized by the frozen blob concentration correlation length ξ_c, usually much larger than ξ_r. At scales larger than ξ_c the system looks homogeneous. Only in the reaction bath ξ_c is equal to ξ_r. The appreciable enhancement of concentration inhomogeneities upon swelling is essentially expected near the percolation threshold of the blobs. It should be stressed that at this threshold the cross-link density is still low (since $p_c \simeq 0.2$), and even if the cross-links were distributed regularly the gel would swell appreciably, as an average strand between cross-links would contain about five blobs.

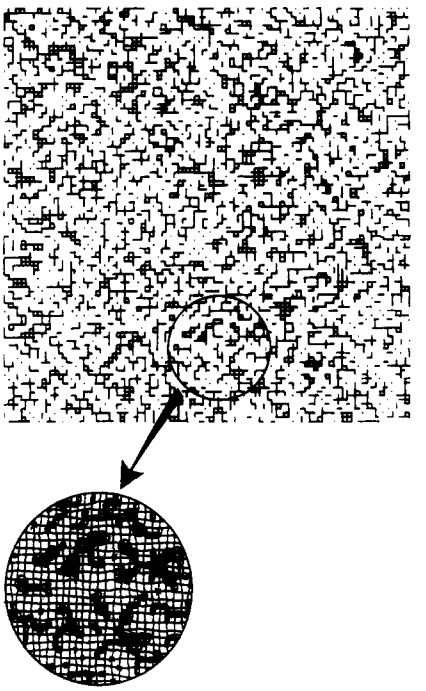

Figure 1. Schematic representation of a randomly cross-linked polymer solution, in the reaction bath well above the gel point. Points and bonds represent respectively isolated cross-links and "frozen blobs". Chains are not drawn on the figure. All points and clusters are linked by chains as shown schematically in the insert. The situation considered here corresponds to an advancement of the reaction just below the frozen blob percolation threshold. The clusters have been obtained by putting points at random on a lattice with a computer. First neighbors on the lattice have then been connected.

Let us examine more precisely the change of concentration fluctuations during the dilution process. When the gel swells, the frozen blob clusters rearrange themselves in a complex way. Small clusters are expelled from bigger ones creating regions of low concentration. The correlation length ξ_c can be now viewed as the typical size of clusters that are not entangled with smaller ones. Obviously this is also the typical size of holes in the frozen blob clusters. Holes thus created are part of the interstitial medium. The dilution process resembles a random unpacking and rearrangement of Russian dolls. Because of the polydispersity of the clusters, we expect a very strong dependence of ξ_c on the dilution degree (or the gel concentration φ), much stronger than in classical monodisperse semidilute solutions. An analogy with the dilution of percolation clusters would suggest $\xi_c \simeq \varphi^{-m}$ with $m \simeq 5/3$.[16] Although we do not expect the analogy to be strict, the important point is that the exponent m has to be high. The very mechanism of swelling leads

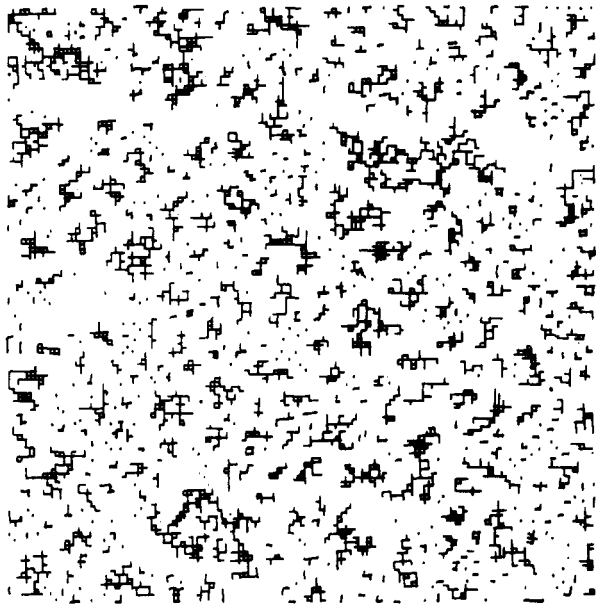

Figure 2. Swelling of the network introduced in Figure 1. Large-scale inhomogeneities appear during the swelling process because frozen blob clusters swell less than the interstitial medium formed by chains connecting frozen blob clusters. For the simplicity of the picture we neglected the deformation and rotation of the frozen blob clusters. It should be stressed that in three dimensions clusters interpenetrate much more. Frozen blob clusters have exactly the same size as in Figure 1. Note that this is a "handmade simulation". The picture has been obtained by, first, magnifying Figure 1 with a photocopy machine. Then, the magnified clusters were replaced by their equivalent of the original size, disposed in such a way that the "center of mass" of the large and the small roughly coincide (except for those of the edges, which have been aligned).

also to an excess scattering with respect to a semidilute solution of linear chains of concentration φ. This excess scattering comes from the "contrast" (arising from the monomer concentration difference) between frozen blob clusters and holes created by the dilution. In this partly interpenetrated regime, the scattered intensity in the forward direction $I(q\rightarrow 0)$ (q denoting the scattering vector amplitude) is expected to depend on the monomer concentration as

$$I(q=0) \simeq \varphi^{-n} \qquad (n > 0) \tag{1}$$

This is a crucial point: the partial separation of frozen blob clusters during the dilution process leads to a strong increase of the scattering intensity. Again a simple analogy with a semidilute solution of polydisperse percolation clusters suggests $n \simeq 5/3$.[16] (We will come back to this point later.) Although the analogy may be of limited validity for our gel system, one still expects a high value for n because of polydispersity effects. The variation of φ should certainly be much stronger than for a semidilute solution of linear chains (when $n \simeq 1/4$).

III. Scattering by a Stretched Gel

What happens when such a swollen gel is uniaxially stretched? We deal here with gels whose frozen blob clusters are only partially separated (and characterized by a certain value of the correlation length $\xi_c(\varphi)$). If we consider the direction parallel to the deformation axis, the frozen blob clusters look as if they were diluted upon stretching, since they are expected to deform less than the interstitial medium. This is the main assumption of the model (Figure 3). On the other hand, along the perpendicular axis, the degree of interpenetration of the clusters increases, since, under deformation, the volume of the gel remains essentially unchanged. As a result, ξ_c becomes anisotropic: $\xi_c^{\parallel} > \xi_c > \xi_c^{\perp}$ and also the scattering intensity exceeds that in the perpendicular direction (Figure 4). This stronger scattering along the stretching direction is a very peculiar feature of nonhomogeneously swollen gels. For uniform gels, on the basis of classical elasticity models, Onuki[11] predicts a completely opposite effect of the intensity lowered in the parallel direction.

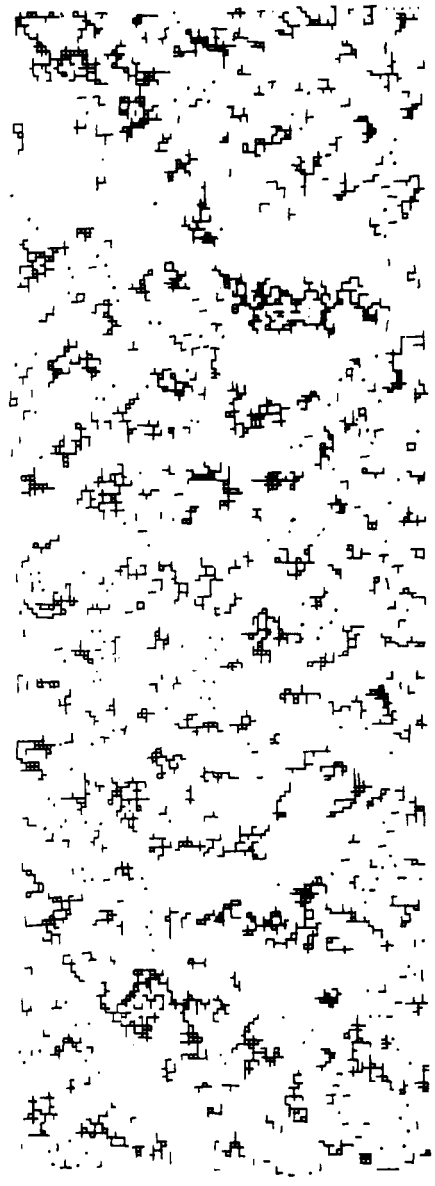

Figure 3. Uniaxially stretched swollen gel of Figure 2. Anisotropy in the shape of inhomogeneities appears during the deformation process because the interstitial medium (not represented in the figure) deforms much more than the frozen blob clusters. For the sake of simplicity in this schematic representation we have ignored the possible deformation and rotation of frozen blob clusters. This anisotropy is the source of unusual "butterfly" scattering patterns: density fluctuations are the largest along the stretching direction. Frozen blob clusters have exactly the same size as in Figures 1 and 2. This figure is again the result of a handmade simulation. It has been obtained by, first, deforming Figure 2 with a photocopy machine ($\lambda y = 2$, $\lambda z = 1/2^{1/2}$). The deformed clusters were then replaced by underformed ones as in Figure 2.

An analogy with classical semidilute polymer solutions suggests a simple form for the scattering spectrum $I(q)$. For scattering vector amplitudes q such that $1/\xi_c < q < 1/\xi_r$, we mainly probe the "intermediate" distance

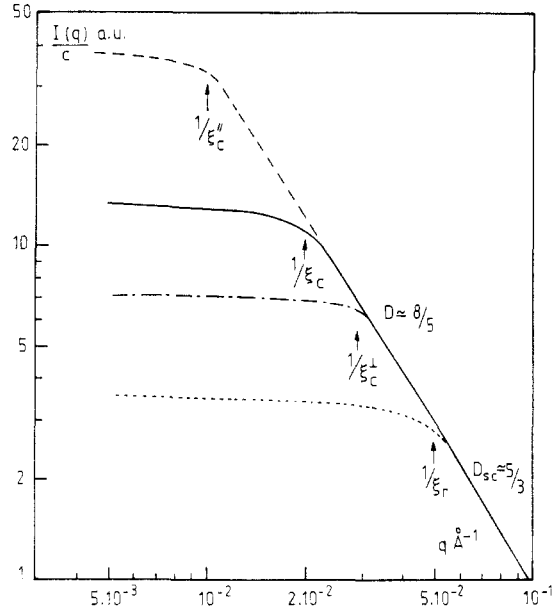

Figure 4. Scattered intensity spectrum (c denotes the polymer concentration): (- - -) in the reaction bath; (—) in a swollen gel; in a uniaxially stretched swollen gel; (– – –) parallel; (– · –) perpendicular. As explained in the text, in the case of the elongated gel, a certain anisotropy, not represented on the figure, should appear at large q values (typically for $q > 1/\xi_c$) as a result of the extension of the interstitial medium.

scales, i.e., the inside of the frozen blob clusters, which are expected to remain almost isotropic. We thus expect

$$I(q,\alpha) \simeq \varphi/q^D \quad \text{for} \quad 1/\xi_c^{\parallel} < q < 1/\xi_r \tag{2}$$

where α is the angle between the scattering vector q and the elongation axis. The exponent D is related to the fractal dimension of the frozen blob clusters and to their polydispersity. ξ_r denotes the correlation length in the reaction bath, i.e., roughly the frozen blob size. Analogy with percolation clusters[16] suggests $D \simeq 8/5$.

Small scattering vectors probe large distances and are sensitive to the anisotropy of concentration fluctuations characterized by the anisotropic correlation length $\xi_c(\alpha)$. We neglect here the elastic effects (cf. Appendix). By analogy with critical phenomena in anisotropic systems[17] and the blob model of polymer solutions[18] we propose an interpolation formula

$$I(q,\alpha) \simeq \frac{\varphi \xi_c^{\,D}(\alpha)}{1 + g(q,\alpha) q^2 \xi_c^{\,2}(\alpha)} \tag{3}$$

where the crossover function

$$g(q,\alpha) \simeq \frac{1}{1 + [q\xi_c(\alpha)]^{2-D}} \tag{4}$$

assures that at high-q vectors the intensity varies according to (2). Note that $\varphi \xi_c^{\,D}$ is the scattering intensity $q = 0$ of a gas of uncorrelated "blobs" of size ξ_c. In this picture, we neglect elastic effects and we emphasize the change of the number of correlated scatterers ("mass of the blob"): the stretching partially separates clusters in the parallel direction and partially interpenetrates them in the perpendicular direction. In a homogeneous medium, the number of correlated scatterers depends only on the average concentration, which does not change during a uniaxial stretching.

To be complete, we should mention a third regime, $q > 1/\xi_c$, where one probes as well the correlations inside the frozen blobs and inside the interstitial medium. The frozen blobs remain essentially isotropic and scatter like $q^{-1/\nu}$, ν being the classical excluded-volume exponent[18] ($\simeq 3/5$). Conversely, the interstitial medium, which is formed of elongated chains connecting the clusters and is responsible for the elastic properties of the gel, should exhibit a certain anisotropy. It is expected to be well described by the usual rubber elasticity theory: intensity is lowered in the parallel direction and increased in the perpendicular one. Isointensity curves should be elliptical (with the large axis perpendicular to the stretching direction). The total scattering is the sum of the two contributions. In summary, for $q > 1/\xi_r$, one expects a moderate anisotropy and an absolute intensity not very different from the isotropic one, in any direction.

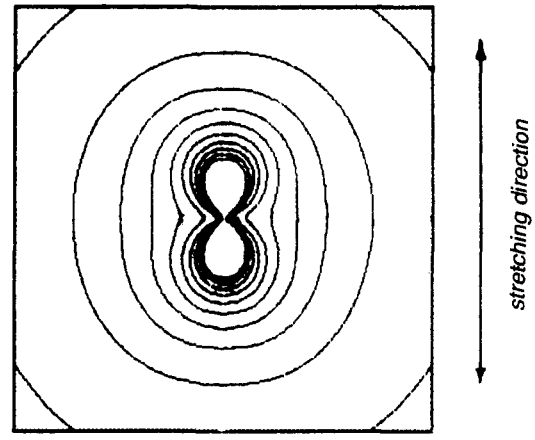

Figure 5. Isointensity curves for a uniaxially stretched gel calculated for $\lambda = 1.2$ and $\xi_c = 50$ Å. The scattering vector amplitude $|\tilde{q}|$ varies between 0 and 10^{-1} Å^{-1}. Even for such a small deformation the anisotropy of the scattering spectrum is strong.

One should remark that the exponents m characterizing the variation with monomer concentration of ξ_c and the exponent n characterizing the forward scattering intensity $I(q=0)$ are not independent since $n = mD - 1$. Note that this relation is satisfied in the percolation cluster analogy. Finally a standard elliptic extrapolation (between $\xi_c^{\parallel}$ and $\xi_c^{\perp}$) of the anisotropic correlation length $\xi_c(\alpha)$ yields

$$\frac{1}{\xi_c^{\,2}(\alpha)} = \frac{\cos^2\alpha}{\xi_c^{\parallel\,2}} + \frac{\sin^2\alpha}{\xi_c^{\perp\,2}} \tag{5}$$

At this point, we should estimate how $\xi_c^{\parallel}$ depends on the macroscopic elongation ratio. A precise thermodynamic calculation seems to be beyond our reach at present as we do not know how to construct a detailed statistical theory of swelling of nonhomogeneous gels. The purely geometrical limit case of the separation (without deformation) in the parallel direction of frozen blob clusters upon stretching leads to

$$\xi_c^{\parallel} = \lambda^{3m} \xi_c \tag{6}$$

This is obtained in assuming that the increase of distances by λ in one direction has the same effects on ξ (in this direction) as a dilution by a factor λ^3 (i.e., $(\varphi/\varphi_i) = \lambda^{-3}$). The assumption of volume conservation upon stretching leads to a deformation ratio equal to $\lambda^{-1/2}$ in the perpendicular direction. As a result, one expects in this direction

$$\xi_c^{\perp} = \lambda^{-3m/2} \xi_c \tag{7}$$

The overall variation of the scattering spectrum is thus expected to be very strong. Figure 5 shows that even for a relatively low stretching the butterfly effect may be

quite pronounced. In calculating this scattering spectrum we have neglected the scattering by chains in the interstitial medium.

IV. Concluding Remarks

In summary, we argue that the inhomogeneity in tie-point density, inherent to the gel preparation by random cross-linking, leads to a spatially inhomogeneous deformation of the network. This effect may be responsible for the appearance of butterfly patterns in uniaxially deformed gels, with scattering intensity stronger in the parallel direction for small values of scattering vector amplitude. The important point of the proposed mechanism is the separation of polydisperse more cross-linked clusters, which are supposed to be less deformed than less cross-linked regions. We estimated the effects in a limit case of when the interstitial medium only deforms. We completely neglected both the deformation and the rotation of frozen blob clusters.[19]

A more realistic model would probably lead to modified values of exponents m, n, and D, but still we believe that the anisotropy effects would be qualitatively unaffected.

The proposed mechanism could also contribute to the anisotropy effects observed in gels swollen by labeled chains or even in mixtures of short and long chains where, at intermediate time scales, entangled long chains may form a nonhomogeneous network swollen by relaxed short chains. Other mechanisms are of course possible and have been proposed for such systems.[9,10,20] Systematic experiments on swollen gels prepared by random cross-linking are now under way. It should be noted that in some (rare) cases the heterogeneity of swollen gels may lead to the completely opposite effect of a scattering intensity stronger in the perpendicular direction than in the parallel one. Indeed if upon swelling the frozen blob clusters would be completely separated and find themselves in a dilute regime, further dilution (stretching) would lead to the decrease of concentration fluctuations and of the scattering intensity.

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Appendix

A more fundamental expression of the scattered intensity in the isotropic case for $q < 1/\xi_c$ should exhibit a φ^2 dependence, as a manifestation of an interparticle scattering. This is, for example, the case in the model of light scattering by isotropic gels, derived by Tanaka et al.,[21] where one has

$$I(q=0) \simeq \frac{\varphi^2}{\kappa_{os} + 4/3\mu} \qquad \text{(A1)}$$

where κ_{os} and μ are respectively the osmotic bulk modulus and the shear modulus.

κ_{os} and μ both depend on φ. κ_{os} is mainly governed by the mixing properties of the polymer and the solvent, with a weaker (and negative) contribution of the elasticity. A model of homogeneous gels would predict only a moderate difference between the scattering of a gel and that of a semidilute solution of the same concentration, through a difference in μ and in the elastic contribution of κ_{os}. In the case of heterogeneous gels, one expects a large difference with the semidilute solution of same concentration, because the system contains frozen polymer density fluctuations, which give rise to a strong additional scattering.

In the case of anisotropic gels, the physics of the difference between homogeneous and heterogeneous systems is basically the same. Onuki[11] discussed essentially the change upon stretching of the equivalent of μ. In the present work, we adopt the view that the dominant contribution to the scattering comes from the frozen character of the concentration fluctuations in the stretched gel. Then, the distinction between the osmotic and the elastic contributions has to be revised.

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