Strain Effect on Quasistatic Fluctuations in a Polymer Gel

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We study the scattering properties of a polymer gel uniaxially deformed by anisotropic swelling. Both the light- and neutron-scattering intensities appear to be greatly enhanced along the direction of maximum dilation. Using a scanning light-scattering device, we show that this effect is governed by the "quasistatic" fluctuations, in space, of the polymer concentration, and not by the "thermal" fluctuations.

A large subgroup of the materials called gels are three-dimensional "networks" made of polymer chains weakly cross-linked together by covalent bonds and comprising a large proportion of solvent [1–3]. On one hand, therefore, a gel is an almost liquidlike binary mixture, in which some spatial fluctuations of the polymer concentration are constantly rebuilt, because of the thermal motion [3–7] ("gel modes"). On the other hand, it is a soft solid, showing in particular a spectrum of "quasistatic" fluctuations of concentration in space [6–8]. The latter result presumably from local variations of the network structure: One may imagine the juxtaposition of harder than average regions, with a lower degree of swelling, and complementary soft regions, with a larger degree of swelling. However, the solidlike and the liquidlike characters are quite entangled and it is sometimes difficult to decide whether a given property of a gel is governed primarily by the first or the second feature. This question arises when considering uniaxially deformed gels, which behave as if they were driven close to a phase transition by the applied strain. It has indeed been found that the intensity of neutrons scattered by elongated gels at small angle (the solvent being labeled) is greatly enhanced along the direction of stretching [9]. One possible explanation [10] of the phenomenon is that the "thermal" fluctuations of concentration are amplified strongly along the direction of elongation. An opposite explanation [11–13] would be that the observed behavior originates from a change of profile of the quasistatic fluctuations.

This question is open and can be answered by an experiment. In this Letter, we report on light-scattering measurements which aim to discriminate between these two options. To this end, one wishes to separate the two contributions to the intensity $I(\mathbf{q})$ scattered by a deformed gel: $I_F(\mathbf{q})$, associated with the dynamical concentration fluctuations and $I_{QS}(\mathbf{q})$, related to the quasistatic concentration fluctuations [q denotes the scattering vector of amplitude $q = 4\pi/\lambda \sin(\theta/2)$, λ the wavelength in the medium, and θ the scattering angle]. One can then write [6,7,14,15] $I(\mathbf{q}) = I_F(\mathbf{q}) + I_{QS}(\mathbf{q})$. The method which is used involves the scanning of the studied sample in a laser

beam [14,16], a technique which has recently been applied to gels [15,17–20].

Consider the static (i.e., time-averaged) scattering of a beam of coherent light, for a fixed value of q. Assume that the detector's size is less than one coherence area (the coherence area is a measure of the region over which the fluctuations of the scattered field are correlated). Because quasistatic fluctuations of concentration are present in the sample, the scattering intensities given out from various scattering volumes differ significantly from each other [14,15]. This is observed even when the characteristic length scale associated with the static fluctuations is much smaller than the size of the scattering volume. These variations come from the fact that, by scanning the different scattering volumes, one is probing various realizations of the random but nearly frozen arrangement in space of the quasistatic fluctuations [14]. A related phenomenon is the presence of a quasistatic "speckle" pattern, comparable to the speckle observed for glasses (in which the positions of the scatterers are completely frozen). Contrary to the case of glasses, the quasistatic speckle pattern is superimposed on a rapidly fluctuating "background" $I_F(\mathbf{q})$, comparable to the one observed in the case of solutions, and originating from the thermal fluctuations of concentration [3–5]. When scanning over a very large number of different scattering volumes, one gets, for a given q, a set $\{I_i(\mathbf{q})\}$ of measurements of the scattered intensity, from which one can calculate a mean value, the "ensemble average" $\langle I(\mathbf{q})\rangle_E$. $\langle I(\mathbf{q})\rangle_E$ is equivalent to the value measured in conventional light-scattering experiments (i.e., when the detector spans many coherence areas) or in small-angle neutron-scattering experiments. The distribution of intensities $\omega(I(\mathbf{q}))$ over the set was shown to be well described by a truncated exponential [15]:

$$\omega(I(\mathbf{q})) \sim H[I(\mathbf{q}) - I_F(\mathbf{q})] \exp\left\{-\frac{I(\mathbf{q}) - I_F(\mathbf{q})}{\langle I(\mathbf{q})\rangle_E - I_F(\mathbf{q})}\right\},$$

(1)

where $H(x)$ is the Heaviside step function. Thus the "dynamic" scattering $I_F(\mathbf{q})$ can, in principle, be estimated

from a static experiment. At the same time, one can also determine the ensemble-averaged quasistatic scattering $\langle I_{QS}(\mathbf{q})\rangle_E = \langle I(\mathbf{q})\rangle_E - I_F(\mathbf{q})$.

In order to perform such light-scattering experiments on a deformed gel, we initially had to produce virtually dust-free samples. To this end, we prepared poly-dimethylsiloxane (PDMS) networks by end linking low molecular weight chains ($M_n \approx 9200$, $M_w \approx 21\,000$, silane terminated) with tetrafunctional cross-links (silox-ane tetramers carrying four vinyl groups). This mixture (plus a catalyst [21]) was filtered and poured into a polypropylene mold for obtaining sheets of rubber of controlled thickness. The reaction occurred upon heating. The networks obtained were swollen, washed carefully, dried, and finally reswollen with an appropriate amount of filtered toluene, in order to reach a polymer volume fraction $\phi = 0.256$ (i.e., swelling degree $Q = 1/\phi = 3.9$; swelling degree at saturation Q_{max} 5.5 $\pm$ 0.25). An-other requirement was to impose on the gel a very stable uniaxial strain (over several days). Mechanical stretching of the sample, as for the previous small-angle neutron-scattering experiments [9], was found to be difficult to achieve satisfactorily on the relatively thick samples required by the light-scattering experiment (≈ 5 mm, to avoid problems arising from reflection of light on the edges). Therefore we preferred to perform an anisotropic swelling experiment [22]. An ellipse (major and minor axis, respectively, equal to 20 and 10 mm) was cut in the sheet of rubber of 3.7 mm thickness. This sample was put into a cell having the shape of a flat cylinder (diameter, 25 mm; thickness, 4.62 mm), which was filled with toluene. The sample absorbed the solvent and fitted the walls of the cell. The deformation ratios, with respect to the dry state, along the minor axis, the major axis, and the thickness, respectively, were $\alpha_m = 2.5$, $\alpha_M = 1.25$, and $\alpha_{th} = 1.25$. The swelling ratio $Q = 3.9$ corresponds to an average deformation in every direction of $\alpha_{av} = 1.57$. Thus, in the deformed state at $Q = 3.9$, the gel was extended along the direction of the minor axis by a factor $\Lambda = \alpha_m/\alpha_{av} = 1.58$ with respect to the isotropically swollen state. Along the two perpendicular directions (those of the major axis and of the thickness), the sample was compressed by a factor $\Lambda' = \alpha_M/\alpha_{av} = 0.80 \approx (1.58)^{-1/2}$. Therefore, the strain imposed on the sample can be compared to a uniaxial stretching by a factor 1.58 at constant volume.

Obviously, it was necessary to check that the phenom-enon which we wanted to study was still observed for such PDMS gels for this anisotropic deformation. To this end, we performed a neutron-scattering experiment on a sample anisotropically swollen, in the same cell, with deuterated toluene (in order to get some "contrast" be-tween the polymer of the gel and the solvent). The wavelength of the neutrons was 6 $\pm$ 0.3 Å. The neutron-scattering intensity was recorded on a bidimensional de-tector set at 6.84 m from the sample. As a result, the range of momentum transfers was $0.006 < q < 0.05$ Å^{-1}.

The spectrum of the gel was normalized by the spectrum of water, both for corrections of detector efficiency and for conversion to absolute units (cm^{-1}). The incoherent part of the signal was calculated from the spectrum of pure deuterated toluene and from that of the PDMS melt, and then subtracted. Some isointensity lines are displayed in Fig. 1. As for mechanically stretched gels [9], they show "butterfly" patterns [21], characteristic of a strong enhancement of the scattering intensity in the direction of elongation.

For the light-scattering measurements, the scattering angle θ was 90°, the scattering plane was horizontal, and the cell windows were set at 45° with respect to the in-cident beam, in such a way that $\mathbf{q}$ was parallel to them ($q = 2.73 \times 10^{-3}$ Å^{-1}). The cell, immersed in a toluene bath, was fitted to a frame such that it could be moved ver-tically along two rails by a stepping motor, but all lateral movement was prevented. 2000 positions of scattering volumes, spanning 10 mm in the gel, were probed (twice each) in a back and forth movement. The measurement time for each position was 10 s. Because of a rotation of the cell within the frame, the extension axis was set either parallel or perpendicular to the scattering vector $\mathbf{q}$. A complete measurement cycle for one sample orientation took 16 h. For a fixed position, the scattered intensity was stable for approximately 500 s. The observed slow drift may be due to heating by the laser. The results are shown in Figs. 2(a) and 2(b). It can be seen immediately that the average scattering intensity of the gel is much stronger in the parallel direction than in the perpendicu-lar one. One finds, respectively, $\langle I^{par}(\mathbf{q})\rangle_E = 31.5 \pm 1.5$ and $\langle I^{perp}(\mathbf{q})\rangle_E = 7 \pm 1.5$ in toluene scattering units (the uncertainty corresponds to different series of sample ex-plorations; it is a measure of the reproducibility). This
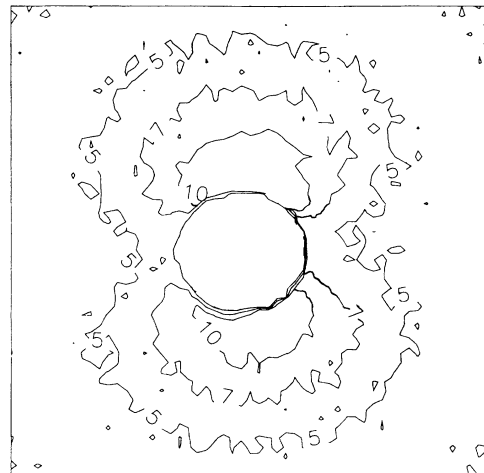

FIG. 1. Experimental isointensity curves [$I(q)$ = 5, 7, 10 cm^{-1}] for a gel deformed uniaxially (in the vertical direction) by a factor $\alpha = 1.58$ (owing to an anisotropic swelling process). The circle in the center indicates the limits of the beam stop. Range of scattering vector amplitude: $0.006 < q < 0.019$ Å^{-1}.

is consistent with the neutron-scattering data (which corresponds to larger values of q). Second, it is clear that the difference between Figs. 2(a) and 2(b) arises primarily from the fraction of the intensity which varies with the position of the scattering volume, that is, the quasistatic intensity.

Direct information about the thermal contribution $I_F(\mathbf{q})$ is obtained from the threshold above which all the data points lie [15] (see Fig. 2). The height $I_{th}(\mathbf{q})$ of the threshold, which is low here compared to $\langle I(\mathbf{q})\rangle_E$, gives, for any geometry, the upper limit for $I_F(\mathbf{q})$. When the detector size is smaller than one coherence area, one has $I_{th}(\mathbf{q}) = I_F(\mathbf{q})$, as expressed in Eq. (1). This condition was nearly reached in the present experiment, as was checked by measuring, with the same setup and using an ALV correlator (ALV, Langen, Germany), the normalized self-correlation function of the scattered intensity $g^{(2)}(q,t) = \langle I(\mathbf{q},0)I(\mathbf{q},t)\rangle/\langle I(\mathbf{q},0)\rangle^2$ for a reference solution giving a pure homodyne signal. One has [14] $g^{(2)}(q,t) = 1 + |\beta f(q,t)|^2$, where $f(q,t)$ is the intermediate scattering function and β is a spatial coherence factor which depends largely on the number of coherence areas seen by the detector ($\beta = 1$ for one coherence area). We estimated $\beta = 0.97 \pm 0.02$ from the limit
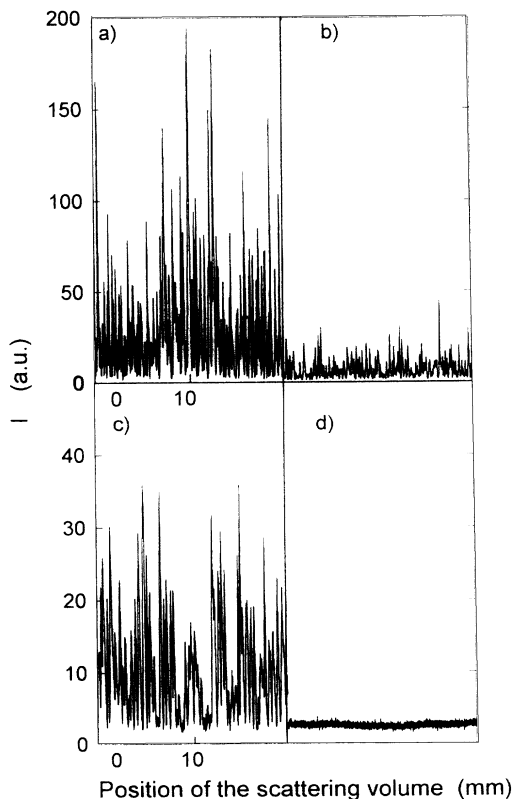

FIG. 2. Scattering intensities as a function of the position of the scattering volume for $q = 2.73 \times 10^{-3}$ Å^{-1}. (a) Deformed gel and scattering vector $\mathbf{q}$ parallel to the elongation axis; (b) deformed gel and scattering vector $\mathbf{q}$ perpendicular to the elongation axis; (c) isotropic gel of same concentration; (d) semidilute solution of same concentration.

$g^{(2)}(q,t \to 0)$, given that $f(q,0) = 1$. Thus $I_F(\mathbf{q})$ must be very close to $I_{th}(\mathbf{q})$. Since $I_{th}(\mathbf{q})$ remains nearly the same [see Figs. 2(a) and 2(b)], the change in $I_F(\mathbf{q})$ from the parallel to the perpendicular configuration, if it exists, can only be very small.

We also studied with the same setup two similar systems: an identical but isotropically swollen gel and a filtered semidilute solution of linear PDMS ($M_n = 72\,000$), both at the same concentration. The results are shown in Figs. 2(c) and 2(d). For the isotropic gel, the average value $\langle I^{iso}(\mathbf{q})\rangle_E$ is found equal to 10.4, that is, intermediate between the parallel and perpendicular values. The threshold $I_{th}(\mathbf{q})$ is located approximately at the same height as for the deformed gel. In the case of the solution, there are no significant variations with respect to the position of the scattering volume. Thus, as expected for a true liquid, all the scattering intensity $I^{sol}(\mathbf{q}) = 2.2 \pm 0.2$ arises from thermal fluctuations. Note that in addition $I^{sol}(\mathbf{q})$ is very close to $I_{th}(\mathbf{q})$.

More specifically, we found that the distributions of the intensities corresponding to Figs. 2(a)–2(c) are well described by truncated exponentials similar to the one of Eq. (1) [$I_F(\mathbf{q})$ being replaced for generality by $I_{th}(\mathbf{q})$]. An example is displayed in Fig. 3, where the data corresponding to the parallel direction are presented in a semilogarithmic representation and can be seen to give a good fit to a straight line. For clarity, the points corresponding to very low intensities are removed and are shown in the inset, using a linear scale. The cutoff corresponding to the threshold $I_{th}^{par}(\mathbf{q})$ is clearly visible. For the isotropic gel and the deformed gel for both orientations of $\mathbf{q}$, we obtain, respectively, the following fit parameters: $I_{th}^{iso}(\mathbf{q}) = 2.4 \pm 1$,
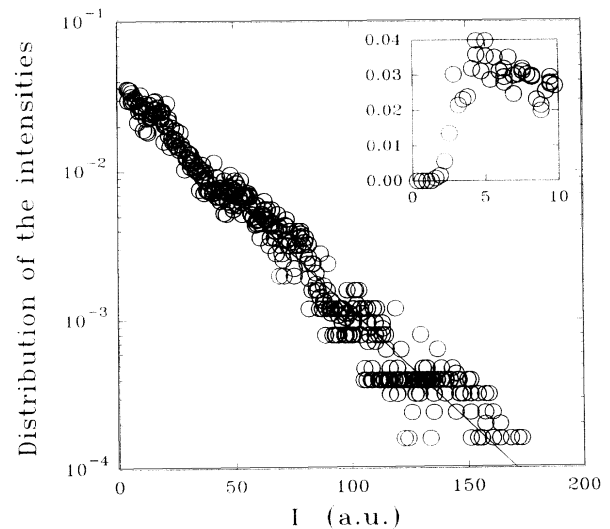

FIG. 3. Distribution of the scattering intensities as a function of the scattering intensities, on a semilogarithmic scale, for the deformed gel with $\mathbf{q}$ parallel to the elongation axis. The points corresponding to the lower intensities have been removed for clarity and are displayed in the inset, on a linear scale.

$I_{th}^{par}(\mathbf{q}) = 2.4 \pm 1$, $I_{th}^{perp}(\mathbf{q}) = 2.2 \pm 0.5$, $\langle I^{iso}(\mathbf{q})\rangle_E - I_{th}^{iso}(\mathbf{q}) = 8.8 \pm 1$, $\langle I^{par}(\mathbf{q})\rangle_E - I_{th}^{par}(\mathbf{q}) = 28 \pm 1$, and $\langle I^{perp}(\mathbf{q})\rangle_E - I_{th}^{perp}(\mathbf{q}) = 5.8 \pm 1$. This analysis therefore confirms that, under strain, there is no significant change of $I_{th}(\mathbf{q})$, which must be virtually equal to $I_F(\mathbf{q})$. Between the parallel and the perpendicular configurations, the major change is an enhancement of $\langle I_q\rangle_E - I_{th}(\mathbf{q})$, which is practically equal to the quasistatic scattering $\langle I_{QS}(\mathbf{q})\rangle$. Thus the latter may be viewed as being superimposed over the thermal scattering from gel modes, which seems to be weakly affected by the strain.

In order to investigate the dynamics of these gel modes, we measured the intensity self-correlation function $g^{(2)}(\mathbf{q}, t)$, in parallel and perpendicular directions, over a set of 125 scattering volume positions, with an aperture of the detector larger than for the static experiments. To build each correlation function, the intensity was recorded for 500 s. When scanning over various positions i, the functions $g_i^{(2)}(\mathbf{q}, t)$ can be well approximated by $1 + \delta_i \exp(-t/\tau_i)$, where δ_i decreases as $I_i(\mathbf{q})$ increases. For each $\mathbf{q}$ orientation, τ_i converges rapidly, as $I_i(\mathbf{q})$ increases, to a limit τ_1 slightly smaller than $2\tau_s$, where τ_s is the value of the relaxation time found in the opposite limit of the lowest intensities. This factor 2 in the relaxation times agrees well with a progressive heterodyning of the signal from the gel modes by the quasistatic part of the intensity $I_{QS}(\mathbf{q})$ of the signal as I_i increases [6,18]. Consequently, we calculated a collective diffusion coefficient $D_c = 1/\tau_1 q^2$ from this limit for both configurations. We found $D_c^{par} = 2.8 \times 10^{-6}$ cm^2 s^{-1} and $D_c^{perp} = 2.3 \times 10^{-6}$ cm^2 s^{-1}, in the parallel and perpendicular directions, respectively. In the case of the isotropic gel of the same polymer concentration, we found, using the same procedure, $D_c^{iso} = 2.4 \times 10^{-6}$ cm^2 s^{-1}. Therefore, the dynamics of the gel modes seems to be slightly accelerated under strain, in the parallel direction, in agreement with previous experiments [23,24] and with theoretical predictions by Onuki [12].

In summary we have shown (i) that a gel deformed by anisotropic swelling exhibits a strong increase of light- or neutron-scattering intensity along the direction of elongation, (ii) that this enhancement arises from a change in the quasistatic part of the intensity, and (iii) that the dynamics of the gel modes is slightly accelerated along the direction of elongation. Such behavior does not agree with the recently predicted [10] amplification under strain of the thermal fluctuations. It is much more consistent with a change of the profile of quasistatic concentration fluctuations, presumably associated with heterogeneous deformation [9,11–13] of the gel. The regions of higher rigidity (with higher concentration) may percolate to some extent into a "superstructure" with correlations on rather large length scales. Under strain, these "harder" regions should deform less than the rest of the gel. Thus the correlations should be "unscreened" in the parallel direction and the ensemble-averaged scattering should be strongly enhanced [11]. Finally, it is interesting to note that a phenomenon governed essentially by "quenched" fluctuations may have features so similar to those of the approach of a phase transition.

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