Elastic Recovery of Gels on Mesoscopic Length Scales. A Photon Correlation Spectroscopy Study

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A stretched rubber band recovers its undeformed shape when externally applied stresses are removed. Similar elastic recovery takes place in polymer gels which are networks of cross-linked polymer chains, permeated by solvent; a macroscopic gel is an elastic solid which can be deformed by the application of external mechanical or thermodynamic forces and which recovers its original shape, when these forces are removed. When one considers the behavior of gels on mesoscopic and microscopic length scales, the analogy with dense rubber breaks down. Scattering experiments reveal that, unlike rubber in which monomer density variations are negligible down to microscopic length scales, dilute gels that appear to be completely homogeneous down to length scales of order 0.1 mm have large density variations on length scales exceeding a few hundred angstroms.[1]

Does a gel respond elastically on such mesoscopic length scales, in the sense that when the external forces are removed, it returns to its initial configuration which is characterized by a particular spatial distribution of density inhomogeneities? For gels in good solvents, a positive answer to this question is expected.[2,3] The situation is more complicated for gels in Θ and poor solvents, and recent computer simulations of floppy two-dimensional networks without excluded volume show that many microscopic configurations are possible for a given network topology.[4]

To study the variation of the density distribution of the gel following the application of a thermodynamic force (temperature change), we carried out photon correlation spectroscopy of light scattered from a gel immersed in a solvent bath. When a coherent laser beam propagates through a medium with randomly distributed scatterers, the resulting pattern of minima and maxima of the intensity, the speckle pattern, is uniquely characteristic of the specific spatial distribution of the scatterers.[5−7] This pattern is an extremely sensitive probe of the variation of the polymer concentration inside the gel on length scales comparable to and exceeding the wavelength of light. Therefore, to check whether a gel has a unique density distribution at each temperature, one can vary the temperature and observe the change in the speckle pattern and then return the temperature to its initial value and compare the final speckle pattern with the initial one. The experimental implementation of this apparently simple procedure for gels in good solvents is nontrivial since good solubility and strong concentration dependence of the index of refraction are usually incompatible. Furthermore, gels in good solvent are athermal; i.e., their equilibrium properties are temperature-independent.[8] As a compromise, we chose to work with polystyrene gels in cyclohexane in which the scattered light intensity can be increased by increasing the concentration of divinylbenzene cross-links.[9,10] Cyclohexane is a moderately good solvent for polystyrene and offers the advantage that solubility varies strongly with temperature in the vicinity of the Θ point (the Θ temperature of the polymer solution is 34.5 °C). Since the crossover from good to Θ solvent takes place when the reduced temperature, $(T - \Theta)/\Theta$, is of order $1/\sqrt{N}$ (N is the number of statistical segments per chain), for $N \simeq 100$, the Θ region extends up to 65 °C.

The gels were prepared by mixing 8 g of cyclohexane with 1.8 g of styrene, 0.2 g of divinylbenzene, and 0.2 g of recrystallized benzoyl peroxide. The components were thoroughly mixed for at least half an hour after which the cuvettes were filled with solution and placed in an oven maintained at 70−75 °C. Gelation was usually completed after 7 h. A 10 mW, polarized, spatially filtered He−Ne laser was used to produce the speckle pattern, and the gel was contained in a square glass cuvette, to minimize the scattering from the gel surface. The cuvette was contained in an equilibrium water bath, whose temperature was actively stabilized to ±0.01 °C, and could be set to any value between 20 and 55 °C. A portion of the speckle pattern was recorded by a CCD camera and frame grabber from which the normalized intensity−intensity correlation, given by

$$C = \frac{\langle I_1 I_2\rangle - \langle I_1\rangle\langle I_2\rangle}{\sqrt{(\langle I_1^{\,2}\rangle - \langle I_1\rangle^2)(\langle I_2^{\,2}\rangle - \langle I_2\rangle^2)}}$$

was calculated. Here $I_{1,2}$ are spatially dependent intensity distributions taken at two different times (1 and 2, respectively), and the brackets represent a spatial average obtained by multiplying the signals at each pixel at two different times and summing over the pixels. The relative total scattered intensity was measured by focusing a large number of speckle spots onto a photodiode. The apparatus was calibrated by measuring the correlation function for a solid diffuse scatterer, which remained at a value of 1 for the duration of the measurement (days).

Measurements on the gel, performed at 45 °C and at 15° scattering angle with respect to the direction of the incident beam, yielded an unexpected result: even when the gel was kept at constant temperature, the correlation decayed to a limiting value of about 0.3−0.4. The decay time was a rapidly decreasing function of the scattering angle, ranging from tens of hours for scattering at 15° to several minutes for backscattering. This angular dependence is believed to be the result of the relative phase change accrued due to the motion of the scatterer for a given observation direction.

Although the observed speckle patterns change in time even in the absence of any temperature changes, the variation is slow enough to allow us to test the elastic recovery hypothesis. In the case of perfect recovery on mesoscopic length scales, by varying the

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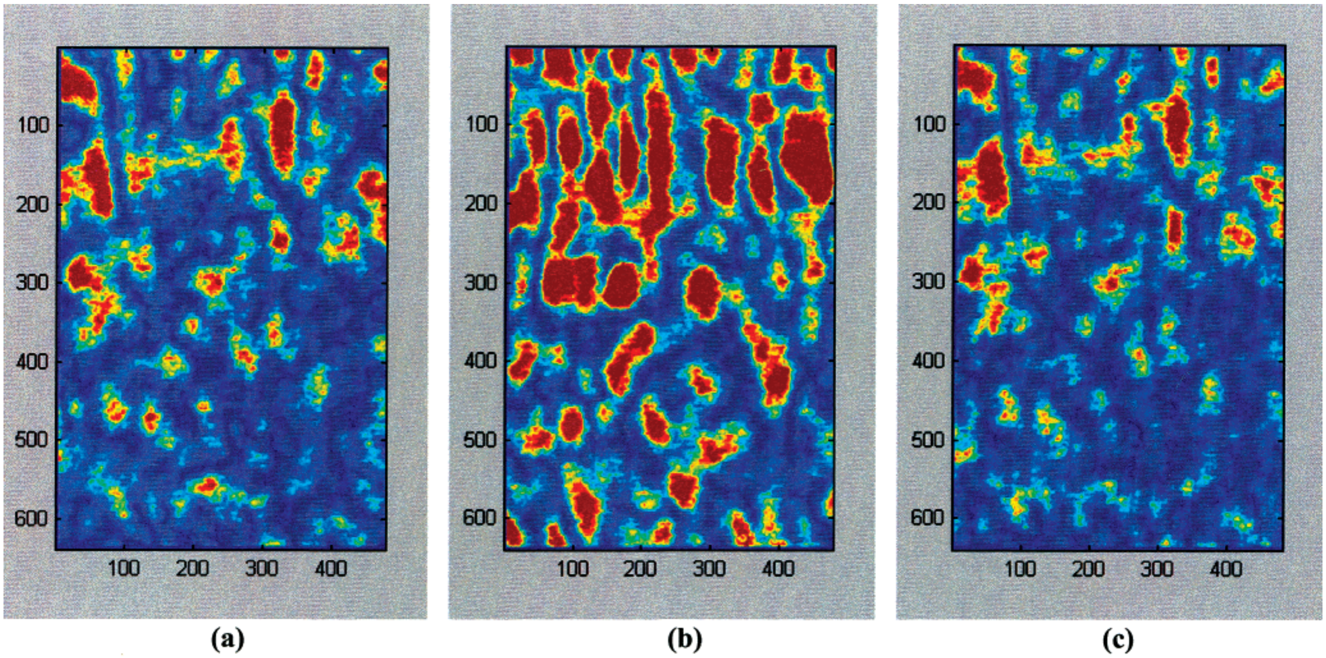

Figure 1. Speckle patterns produced by a He−Ne laser scattered from a 3 mm thick gel near the forward direction: (a) the gel in an initial equilibrium state at 35 °C, (b) after heating by 10 °C, (c) upon reestablishing the initial temperature. High (low) intensity regions are indicated in red (blue).

temperature of the gel sufficiently to cause the correlation to drop to near zero, and subsequently returning to the initial temperature, the correlation should return to 1. Figure 1 shows the actual speckle patterns, recorded at a 15° scattering angle. The first picture was recorded with the gel at 35 °C, the second at 45 °C, and the third speckle pattern was recorded after we returned the temperature to 35 °C. The correlation between the first two speckle patterns is 0.07 while the third speckle pattern is nearly identical to the original one, with a correlation of 0.85. The deviation of the final correlation from a value of 1 is a consequence of the slow change in the speckle pattern even in the absence of any temperature changes. Over the time it took to cycle the temperature, the correlation would drop to 0.85 even if no changes were made in any of the thermodynamic parameters.

In Figures 2 and 3 we show how the correlation drops to a minimum upon a temperature change and returns to a high value after cycling the temperature. In Figure 2 the gel was heated from 35 to 45 °C, resulting in a drop of the correlation to approximately 0.1. (The correlation does not drop to zero due to temperature-independent residual scattering from windows, cuvette surfaces, etc.) As the temperature is brought back to its initial value, the correlation also returns to what it would have been without any temperature change. The correlation follows the temperature to a very high degree and is, in a sense, a very accurate relative thermometer.

In Figure 3 we again show the return of the correlation function to near its initial value, but in this case the temperature change was negative and the gel was cooled from 35 to 25 °C, below the Θ point. The change of state is more dramatic in this case, since sufficiently below the Θ temperature, polystyrene is no longer soluble in cyclohexane and, given enough time, the gel will expel the solvent and collapse.[11] As the gel is heated back to its original temperature, the network reabsorbs the solvent and swells, resulting in a correlation which is close to the value we would have obtained without the collapse.

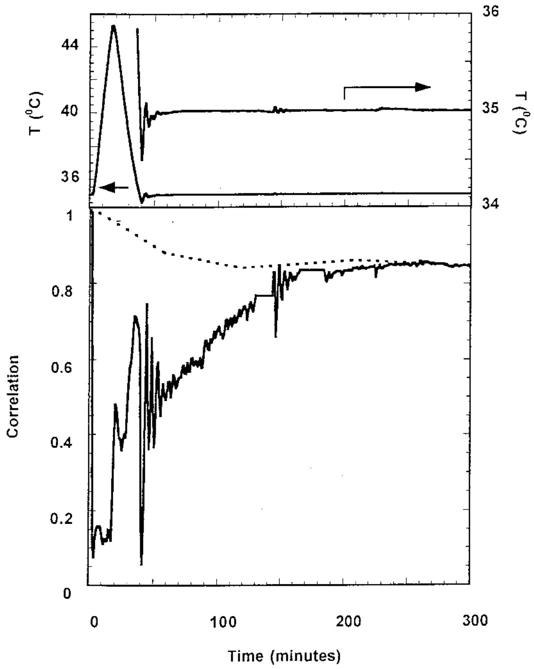

Figure 2. Correlation as a function of time, near the forward direction, for a gel in stationary thermal equilibrium (dotted curve). The solid curve is the correlation when the gel is heated and cooled back to the initial temperature. The time-dependent temperature of the water bath surrounding the gel is shown on a coarse and fine scale at the top of the figure. The spikes in the correlation actually correspond to very small fluctuations in the temperature.

In summary, we observed that upon a cyclic variation of the temperature the speckle pattern almost returns to its original form, and since this pattern is an extremely sensitive probe of the local concentration in the gel on length scales exceeding the wavelength of light, we conclude that the gel undergoes nearly com-

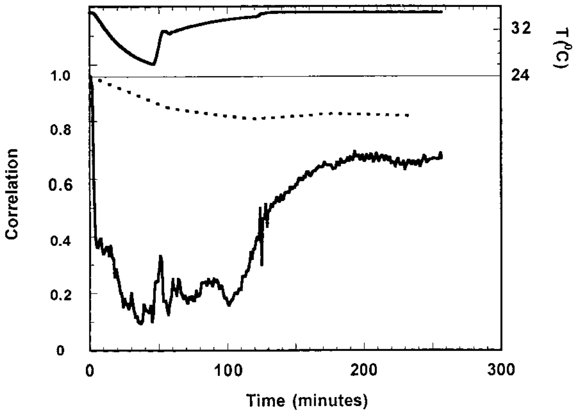

Figure 3. Correlation as a function of time, near the forward direction, for a gel cooled below the Θ point and returned to the initial temperature. The dotted line shows the decrease in correlation for an undisturbed gel.

plete elastic recovery on these length scales. We also observed a slow variation of the speckle pattern with time, even in the absence of any measurable variation of the temperature. Although unexpected, the observation of slow variation of light scattering from gels is not unprecedented; slow reorganization of domains of several microns size was reported in a recent laser scanning confocal microscopy study on NIPA gels prepared in poor solvent.[12]

We would like to propose a possible explanation of the time dependence of the speckle patterns. Note that while static concentration inhomogeneities are always expected in gels,[13] even under conditions of cross-linking by irradiation in good solvent, such inhomogeneities have characteristic length scales comparable to the average mesh size of the network ($\leq$100 Å) and cannot be observed by light scattering methods. The observation of speckle patterns implies the existence of concentration inhomogeneities on much larger length scales, at least of the order of several thousand angstroms. Such large-scale heterogeneity can be produced by the following mechanism. When a gel is formed in the reaction bath, the reaction takes place in a mixture of monomers, cross-linkers, and solvent molecules. Under most conditions, these components do not form an ideal mixture, and the cross-linking reaction takes place in parallel with phase separation. As a result, the mixture is “frozen” in some intermediate stage of the phase separation process, and one obtains a network, in which cross-link-rich clusters of short polymers are surrounded by dilute, swollen regions of predominantly long chains. (This conclusion is supported by visual observation of turbidity during gelation at high concentrations of cross-linker.[14]) Since the monomer and cross-link concentrations in our experiments were chosen on the basis of the requirement that the gel produces sufficiently strong light scattering, the characteristic length scale of inhomogeneities in our gels is at least of the order of the wavelength of visible light.

When temperature is changed, the relative change in the solubility of the dense and the dilute regions gives rise to thermodynamic forces that lead to the reorganization of the network. The fast change of the speckle pattern with changing temperature is produced by local rearrangement of the interface between the polymer-dense and the polymer-dilute regions. This new state is metastable with respect to further coarsening which is driven by surface tension and which occurs through the extremely slow process of coalescence of dense clusters. However, since a gel is a continuous solid, such coarsening can take place only through the reorganization of the entire network. Taking a typical value of the cooperative diffusion constant 10^{-7} cm/s^2 and gel dimensions 1 cm, the lower bound for the time scale of such reorganization is of order 10^7 s. We conclude that the gel does not achieve equilibrium with respect to such slow processes on experimentally relevant time scales and that this continuing reorganization is responsible for the observed anomalously slow decay of the correlation of the speckle patterns.

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References and Notes

(1) Bastide, J.; Candau, S. J. In *Physical Properties of Gels*; Cohen-Addad, J. P., Ed.; Wiley: Chichester, 1996.
(2) Panyukov, S.; Rabin, Y. *Macromolecules* **1996**, *29*, 7960.
(3) Panyukov, S.; Rabin, Y. *Phys. Rep.* **1996**, *269*, 1.
(4) Moussaid, A.; Pusey, P. N.; Slot, J. J. M.; Joosten, J. G. H. *Macromolecules* **1999**, *32*, 3774.
(5) Freund, I.; Rosenbluh, M.; Feng, S. *Phys. Rev. Lett.* **1988**, *61*, 2328.
(6) Joosten, J. G. H.; McCarthy, J. L.; Pusey, P. N. *Macromolecules* **1991**, *24*, 6690.
(7) Orkisz, M. Doctoral Dissertation, MIT, 1994.
(8) deGennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(9) Candau, S. J.; Munch, J. P.; Hild, G. *J. Phys. (Paris)* **1980**, *41*, 1031.
(10) Munch, J. P.; Hild, G.; Candau, S. J. *Macromolecules* **1983**, *16*, 71.
(11) Tanaka, T.; Fillmore, D. J. *J. Chem. Phys.* **1979**, *70*, 1214.
(12) Hirokawa, Y.; Jinnai, H.; Nishikawa, Y.; Okamoto, T.; Hashimoto, T. *Macromolecules* **1999**, *32*, 7093.
(13) Shibayama, M. *Macromol. Chem. Phys.* **1998**, *199*, 1.
(14) Bianco-Peled, H., private communication.

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