Macromol. Symp. **2011**, 306-307, 27–32 DOI: 10.1002/masy.201000114

Kinetics of Jammed Systems: PNIPA Gels

Krisztina László,[1] *Andrei Fluerasu,*[2,4] *Abdellatif Moussaïd,*[2,3] *Erik Geissler**[3]

Summary: In the out-of-equilibrium state above the volume phase transition temperature, poly(*N*-isopropyl acrylamide) hydrogels deswell non-diffusively, relaxing instead by a hyperdiffusive mechanism as in jammed systems. X-ray photon correlation spectroscopy is employed to show that the unconventional relaxation properties (linear dependence of the intensity correlation function both on time and on transfer wave vector) are the consequence of uniform deswelling.

Keywords: hydrogels; relaxation; small-angle X-ray scattering (SAXS); stimuli-sensitive polymers

Introduction

A remarkable characteristic feature of disordered crowded systems such as dense colloidal suspensions or glasses is their anomalous relaxation behaviour. These differ from low concentration suspensions, where the Brownian or quasi-Brownian dynamics of the individual constituents generates simple exponential intensity correlation functions in a scattering experiment, and the relaxation rates are diffusive, i.e., of the form $\Gamma = Dq^2$, where q is the momentum transfer and D the diffusion coefficient. Anomalous relaxation mechanisms, by contrast, display non-exponential correlation functions and non-diffusive dispersion relationships.

Slower-than-exponential decays are widespread. They occur for instance in colloidal glasses, and are usually associated with the fast dynamics of individual constituents surrounded by "cages" composed of their neighbours (β-relaxations). These are explained by established theories, such as mode coupling theory, which also captures the sub-diffusive nature of the dynamics. Faster-than-exponential decays, on the other hand, are still considered extraordinary, even though they have been observed in an increasing number of "glassy" materials.[1–3] In these systems, the correlation functions can usually be described by the Kohlrausch-Williams-Watts (KWW) compressed exponential form – $\exp(-(\Gamma t)^n)$ – where $n > 1$ and the relaxation rates Γ exhibit hyper-diffusive dispersion relationships $\Gamma \sim q^p$, with $p = 1$ (ballistic motion) or, more generally, $p < 2$. Two principal microscopic explanations have been suggested for this type of dynamics, which applies to glasses, gels, and more broadly to "jammed materials".[4,5] In the first, due to Bouchaud and Pitard,[6] later developed and investigated by Cipelletti et al. [5] in a variety of systems using dynamic light scattering (DLS), point sources of dipolar stress, appearing when the system is temporarily arrested in a non-equilibrium state, create strain field relaxations that are characteristic of the induced velocities. These are faster than those associated with thermal diffusion (which is vanishingly small in systems composed of

---

[1] Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, Hungary
E-mail: klaszlo@mail.bme.hu, Fax: (+36) 1-463-3767
[2] European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble cedex, France
E-mail: a.moussaid@esrf.fr
[3] Laboratoire Interdisciplinaire de Physique, CNRS UMR 5588, Université J. Fourier de Grenoble, BP 87, F-38402 St Martin d'Hères cedex, France
E-mail: erik.geissler@ujf-grenoble.fr; Fax: (+33) 476 635495
[4] Present address: NSLS-II, Brookhaven National Laboratory, Upton, NY 11973-5000, USA
E-mail: fluerasu@bnl.gov

macroscopic grains), and hence dominate. This mechanism predicts a KWW exponent $n = 1.5$ and ballistic motion of the constituents, i.e., $p = 1$. A second mechanism that yields dynamics with $n > 1$ involves a continuous time random walk (CTRW) model,[2,7] where individual constituents undergo sequences of "jumps" with a distribution of jump lengths and of wait times before each jump. This model predicts a cross-over from $n = 2$, $p = 1$ at low q to diffusive motion, $n = 1$, $p = 2$ at high q. Recent experimental results from X-ray photon correlation spectroscopy (XPCS)[8] suggest a third picture where the diffusive dynamics of colloidal particles suspended in a polymer solvent at low enough temperatures is masked by another process, e.g., convective motion in the solvent.

The XPCS experiments reported here investigate the dynamics of an out-of-equilibrium system, namely a poly(N-isopropyl acrylamide) (PNIPA) hydrogel undergoing deswelling. It was reported earlier[9] that above the volume phase transition (VPT) PNIPA gels exhibit the signature of jamming: the relaxation rates measured by XPCS display linear dispersion relationships ($\Gamma \propto q$) and compressed exponential relaxations ($n > 1$). Such a non-granular material is exceptional among jamming systems. As in other jammed systems,[1–3] however, the origin of the linear q dependence of Γ remains an open question. Here we report further observations on PNIPA hydrogels, and interpret the results quantitatively in terms of a simple model for which the correlation decay is the consequence of uniform deswelling of the whole polymer matrix.

Results and Discussion

PNIPA hydrogels belong to a class of environmentally sensitive systems that display a VPT at a critical temperature $T_{\mathrm{VPT}} \approx 34\,^{\circ}\mathrm{C}$, above which they shrink by expelling the solvent. This stimulus-responsive feature has inspired numerous investigations into their swelling/deswelling kinetics.[10,11] At the molecular level, however, the kinetics of this system is poorly understood. Microphase separation, which appears at the VPT, scatters visible light so strongly that observations of the bulk material by standard DLS are severely hampered. X-rays, however, offer a means of investigating the internal structure. In the small angle X-ray scattering (SAXS) range, the principal source of scattering in PNIPA gels above the VPT is the polymer surfaces that form upon microphase separation.[12] The existence of these surfaces is apparent from the power law behaviour shown in Figure 1, where the scattered intensity $I(q)$ decreases as q^{-4}.[13] At higher values of q in this figure, the signal from the water in the gel contributes significantly and must be subtracted to yield that of the polymer alone (lower curve). The broad peak denoted by an arrow at $q^* \approx 0.56$ Å^{-1} reflects short-range order in the separation between neighbouring polymer chains. The breadth of the peak is evidence that long-range liquid crystalline order does not prevail in the collapsed polymer phase.

XPCS measurements were made on beam line ID10A at the European Synchrotron Radiation Facility, Grenoble, France, as described in reference.[9]

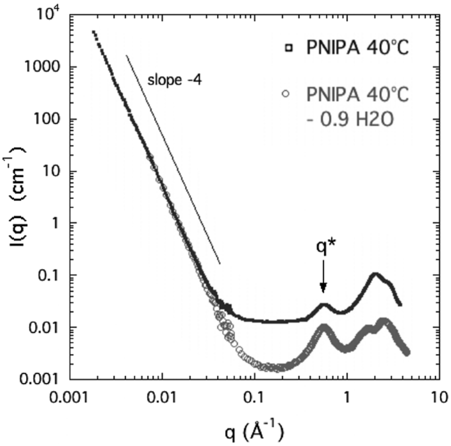

Figure 1.
SAXS response of a PNIPA hydrogel at 40 °C. Upper curve: uncorrected signal; lower curve, after subtraction of the signal of pure water. Arrow indicates position of interchain peak.

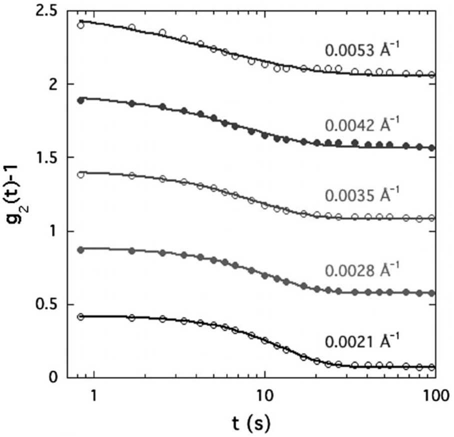

Figure 2.
XPCS intensity correlation functions of a deswelling PNIPA gel at 50 °C for different values of transfer momentum *q*. Continuous lines are fits to $g_2(t)$-1 $\propto$ exp[-$(\Gamma t)^n$]. Successive curves vertically offset by 0.5.

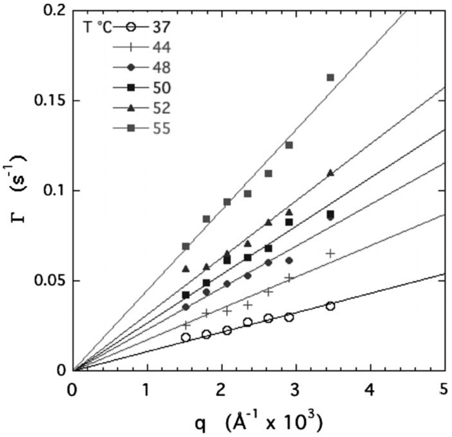

Figure 3.
q-dependence of XPCS relaxation rates Γ as a function of temperature.

Figure 2 shows ensemble averaged intensity correlation functions $g_2(t)$-1 measured in a PNIPA gel undergoing slow collapse at 50 °C. The lines through the data are fits to the KWW form $\exp(-(\Gamma t)^n)$, where the exponent $n \approx 1.4$ expresses the sharp, faster-than-exponential decrease of the decay. The incomplete decay to zero of $g_2(t)$-1 in Figure 2 is due to residual parasitic scattering from the guard slits. Data accumulation times at each temperature were about two thousand seconds.

The variation of the decay rate Γ with q at various temperatures $T > T_{VTP}$ is shown in Figure 3. At each temperature, the linear relationship $\Gamma \propto q$ confirms the hyper-diffusive nature of the deswelling motion. This non-diffusive behaviour of PNIPA gels is not widely recognized.

To understand the context of these results, we note that in photon correlation experiments, when the sample moves uniformly at velocity u perpendicular to the beam, the rate at which a given scattering pattern is replaced is u/R, where R is the radius of the incident beam at the sample. The intensity correlation function therefore decays proportionally to (1- ut/R). When the beam is divergent, an additional factor (1- $ut/2R_0$) applies, where R_0 is the radius of the defining pinhole. Neither of these contributions depends on q, and their effect in the present measurements is too small to be observed.

All the gels were prepared with a molar ratio of N-isopropyl acrylamide to cross-linker (N,N′-methylene bisacrylamide) 150:1. The samples were synthesized in the form of disks of swollen diameter $d_0 \approx 7$ mm and thickness 1.5 mm, with different degrees of inhomogeneity, as described elsewhere.[14,15]

To shed light on the nature of the gel motion, macroscopic measurements of deswelling were made on disks of three different PNIPA gel disks by immersing them in a water bath at 50 °C and measuring their diameter d with a video camera as a function of elapsed time t.

The macroscopic responses, shown in Figure 4, illustrate the fact that the deswelling kinetics of PNIPA hydrogels above the volume phase transition temperature T_{VPT} depends sensitively on the amount of structural inhomogeneities present in the network.[11] Essentially, two types of behaviour are observed. Gels containing small amounts of cross-linker deswell extremely slowly, but above a given cross-link content an abrupt increase in their deswelling rate is observed. Although the reason for the change in behaviour is

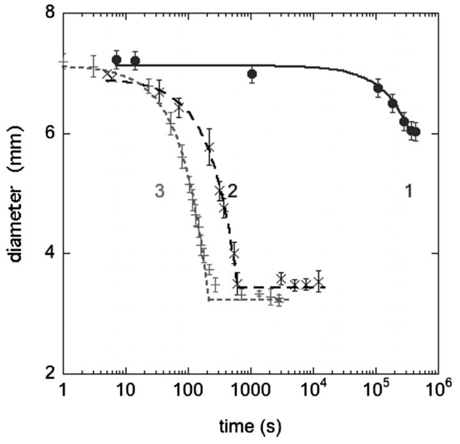

Figure 4.
Time dependence of the diameter *d* of PNIPA hydrogel disks during macroscopic deswelling at 50 °C for samples of increasing inhomogeneity 1, 2 and 3. Lines are fits of the data to $d = d_0 - vt$, where v is the velocity of the disk at its outer diameter.

not well understood, network inhomogeneities appear to limit the formation of interlocking network chains, thereby facilitating their relative motion. Network inhomogeneities that promote this switch in behaviour can also be generated by copolymerizing the PNIPA with bulky molecules, or even simply by drying the gels and allowing them to re-swell. In the latter case, the formation of hydrogen bonds in the collapsed state suffices to prevent extended ordering of the chains above T_{VPT}. In Figure 4, sample 1 was washed after synthesis and kept in the swollen state; sample 2 was dried in a desiccator, then reswollen; sample 3 was copolymerized with a crown ether in order to enhance the structural inhomogeneity.[15] For the three PNIPA hydrogels of increasing network inhomogeneity, Figure 4 shows that the disk diameter decreases linearly with time until the equilibrium volume is reached (in the logarithmic scale of this figure, the linear decays appear curved). This linear decay means that the gel deswelling is not diffusive but proceeds instead by uniform isotropic expulsion of the solvent. In such a scenario, all points in the gel approach each other at a uniform velocity

$$\mathbf{v} = \alpha \mathrm{r}, \tag{1}$$

where **r** is the separation between any two points and $\alpha = \nabla \cdot \mathbf{v}$ is the divergence of the velocity. When the deswelling rate is too high, blisters tend to develop at the outer boundary of the gel where the solvent flux is highest.[14] Blisters are not observed in the slowly deswelling gels.[11]

Uniformity of $\nabla \cdot \mathbf{v}$ means that the spatial correlation function of the polymer network at any time, $\gamma(\mathbf{r}, t)$, is the same as that at a later time $t + \tau$, except that **r** is then $\mathbf{r}\text{-}\mathbf{v}\tau = \mathbf{r}(1\text{-}\alpha\tau)$. Since the scattered intensity is the Fourier transform of $\gamma(\mathbf{r}, t)$,

$$I(\mathbf{q}) = \int_0^\infty \gamma(\mathbf{r}, t)\exp(i\mathbf{q}\cdot\mathbf{r})\,d\mathbf{r} \tag{2}$$

it follows that the scattering pattern at $t + \tau$ has the same form as at time t, but the image is enlarged. As the gel shrinks uniformly, the scattering pattern expands uniformly outwards to larger q. Features appearing at **q** at time t thus shift to[16]

$$\mathbf{q}/(1-\alpha\tau) = (\mathbf{q} - \mathbf{q}\alpha\tau)/(1-\alpha\tau)^2 \tag{3}$$

so that the speckles move radially outwards over the detector at a uniform rate

$$\partial \mathrm{q}/\partial \mathrm{t} = q\alpha/(1-\alpha \mathrm{t})^2 \tag{4}$$

In the XPCS arrangement, each detector pixel subtends one coherence area of the scattered radiation, spanning a scattering angle range $\Delta\theta = \lambda/R$. The range of q covered by one pixel is therefore

$$\Delta q = \Delta(2\pi/\lambda)\sin\theta = (2\rho/R) \tag{5}$$

The intensity correlation function, which is determined by the time required for a speckle to migrate over one pixel, is therefore

$$g_2(\tau) - 1 \propto (1 - q\mathrm{R}\alpha\tau/[2\pi(1-\alpha\tau)^2]) \tag{6}$$

In Figure 5 it is seen that Equation 6 provides a reasonable fit to the same intensity correlation functions as already shown in Figure 2.

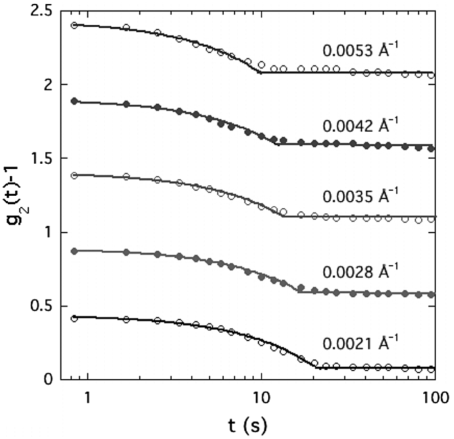

Figure 5.
Same XPCS intensity correlation functions as in Figure 2. Continuous lines are fits to the linear decay of Equation 6.

From Equation 6 it follows that the relaxation rate

$$\Gamma = q\alpha \mathrm{R}/([2\pi(1-\alpha \mathrm{t})^2] \tag{7}$$

reproduces the same linear dependence of Γ on q as that found experimentally in Figure 3.

The XPCS experiment was performed on sample 1 (low inhomogeneity content), for which the measured deswelling rate in Figure 4 is $v = 3.1 \times 10^{-7}$ cm/s, i.e.,

$$\alpha = 4.4 \times 10^{-7}\,\mathrm{s}^{-1} \tag{8}$$

This value may be compared with that obtained from the XPCS measurement at the same temperature (Figure 3), where the beam radius is $R = 7 \times 10^{-4}$ cm, namely

$$\alpha = 2.3 \cdot 10^{-3}\,\mathrm{s}^{-1} \tag{9}$$

The discrepancy between results 8 and 9 is almost 4 orders of magnitude.

In the above comparison, however, the effects of ionisation due to the high intensity X-ray beam required for the XPCS experiment are overlooked. The radiation, which deposits more than 10 Gy/s into the scattering volume, generates free radicals that, as observed in other systems, alter the local network structure.[17] During the XPCS measurements, for example, it was found that the position in the sample where the beam penetrated became dimpled, i.e., partially deswollen, although the rest of the sample remained in the swollen microphase-separated state. In these observations, therefore, the rapid collapse occurs only in the region where the beam passes. For this reason, a more appropriate macroscopic comparison for the XPCS deswelling result is with that of the most inhomogeneous specimen in Figure 4 (sample 3), namely

$$\alpha = 2.6 \cdot 10^{-3}\,\mathrm{s}^{-1} \tag{10}$$

Given the experimental uncertainties, however, the agreement between the values 9 and 10 is probably fortuitously good.

Conclusion

The observations presented here suggest that the linear dependence both on time and on transfer momentum of the intensity correlation function in this jammed system stems from the divergence of the velocity. Although deviations from linearity in the intensity correlation functions become more pronounced at large q (Figure 5), this discrepancy may be caused by departures from affine deformation at short distances in the network.[12] It is also expected that, in general, as the deswelling system approaches equilibrium, α will be a slowly decreasing function of time, yielding correlation functions that become slower with elapsed time. While other types of motion, e.g., laminar flow or rigid body motion, also give rise to linear dispersion relations,[18,19] the decisive evidence for the model presented here comes from the macroscopic observations. It is not unreasonable to expect that the same mechanism also plays a role in other jammed systems undergoing densification (or expansion), notably colloid suspensions. In such suspensions, however, the gravitational field may introduce anisotropy into the motion. The extension of the present formalism to anisotropic conditions is straightforward.

Acknowledgements: We are grateful to K. Kosik for technical help. This work is based on measurements made at the European Synchrotron Radiation Facility on beam lines ID10A and BM02. Support from the EU - Hungarian Government joint fund GVOP-3.2.2 - 2004 -07 - 0006/3.0 and Hungarian National Research Fund (OTKA, grant No. K75182) is thankfully acknowledged.

[1] L. Cipelletti, S. Manley, R. C. Ball, D. Weitz, *Phys. Rev. Lett.* **2000**, *84*, 2275; B. Chung, S. Ramakrishnan, R. Bandyopadhyay, D. Liang, C. F. Zukoski, J. L. Harden, R. L. Leheny, *Phys. Rev. Lett.* **2003**, *96*, 228301.

[2] A. Duri, L. Cipelletti, *Europhys. Lett.* **2006**, *76*, 972.

[3] A. Fluerasu, A. Moussaïd, A. Madsen, A. Schofield, *Phys. Rev. E* **2007**, *76*, 010401(R).

[4] A. J. Liu, S. D. Nagel, *Nature.* **1998**, *396*, 21; V. Trappe, D. A. Weitz, *Phys. Rev. Lett.* **2000**, *85*, 449; P. N. Segre, V. Prasad, A. B. Schofield, D. A. Weitz, *Phys. Rev. Lett.* **2001**, *86*, 6042;

[5] L. Cipelletti, L. Ramos, S. Manley, E. Pitard, D. A. Weitz, E. E. Pashkovski, M. Johansson, *Faraday Discuss.* **2003**, *123*, 237–251.

[6] J. P. Bouchaud, E. Pitard, *Eur. Phys. J. E* **2001**, *6*, 231.

[7] C. Caronna, Y. Chushkin, A. Madsen, A. Cupane, *Phys Rev. Lett.* **2008**, *100*, 055702.

[8] H. Guo, G. Bourret, et al. *Phys. Rev. Lett.* **2009**, *102*, 075702.

[9] E. Geissler, K. Kosik, A. Fluerasu, A. Moussaïd, K. László, *Macromol. Symp.* **2007**, *256*, 73.

[10] K. Sekimoto, N. Suematsu, K. Kawasaki, *Phys. Rev. A* **1989**, *39*, 4912; R. Bansil, G. Liao, P. Falus, *Physica A* **1996**, *231*, 346; M. Shibayama, K. Nagai, *Macromolecules*, **1999**, *32*, 7461; K. Takahashi, T. Takigawa, T. Masuda, *J. Chem. Phys.* **2004**, *120*, 2972.

[11] K. T. Okajima, I. Harada, K. Nishio, S. Hirotsu, *J. Chem. Phys. 116*, 9068. **2002**.

[12] K. László, A. Guillermo, A. Fluerasu, A. Moussaïd, E. Geissler, *Langmuir* **2010**, *26*(6), 4415–4420.

[13] G. Porod, In *Small Angle X-ray Scattering*, O. Glatter, O. Kratky, Eds., Academic, London 1982.

[14] K. László, K. Kosik, C. Rochas, E. Geissler, *Macromolecules* **2003**, *36*, 7771–7776.

[15] K. Kosik, E. Wilk, E. Geissler, K. László, *J. Phys. Chem. B* **2008**, *112*, 1065–1070.

[16] K. László, A. Fluerasu, A. Moussaïd, E. Geissler, *Soft Matter* **2010**, *6*, 4335–4338.

[17] A. M. Hecht, E. Geissler, *Macromolecules* **1987**, *20*, 2485.

[18] B. J. Berne, R. Pecora, *Dynamic Light Scattering*, Wiley-Interscience, New York 1976.

[19] W. I. Goldburg, *Am. J. Phys.* **1999**, *67*(12), 1152.