Osmotic and Longitudinal Moduli of Polymer Gels

Y. Rabin*,[†],[‡] **and A. Onuki**[§]

Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606, Japan, Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel, and Department of Physics, Kyoto University, Kyoto 606, Japan

Received September 8, 1993
Revised Manuscript Received November 14, 1993

A swollen polymer gel is a network of randomly cross-linked polymer chains permeated by a solvent. Macroscopically (on length scales $\gg 1\ \mu$m), gels behave as tenuous solids and their response to *small* deformations can be described by the standard theory of elasticity of solids.[1] On microscopic length scales, on the order of the size of network chains ($\geq$100 Å), they behave as liquids, an observation which has led to the analogy (c^* theorem[2]) between equilibrium swollen gels and semidilute polymer solutions at overlap concentration c^*.

The mesoscopic physics of gels on intermediate length scales (10^2–10^4 Å) has been the subject of many recent light and neutron scattering studies. These experiments led to the discovery of a number of unexpected phenomena, the most spectacular one being the observation of butterfly patterns of SANS isointensity contours.[3] Although there has been a number of theoretical studies on this subject,[4–7] there is still considerable controversy regarding the physical mechanism responsible for the above phenomenon. In this work we deal with a different issue which is of foremost importance to the interpretation of diffuse thermal scattering from gels, namely, with the relation between their osmotic and longitudinal moduli.

Small-angle elastic scattering measures the small-wavevector (**k**) limit of the static structure factor $S(\mathbf{k})$ which is the Fourier transform of the monomer density correlation function. In gels there are two contributions to the scattering intensity: one associated with thermally-driven (annealed) density fluctuations and one associated with the frozen (quenched) heterogeneous structure of a randomly cross-linked network. In light scattering experiments the two components can be separated by time-resolved measurements by monitoring the decay of the two-time intensity correlation function. The situation is more complicated in SANS experiments where the separation of annealed and quenched contributions is done empirically, by assuming a given functional form (usually Gaussian) of the **k**-dependence of the quenched (frozen-in) component.[8] In the following we will assume that the two components can be separated by a reliable procedure and consider only the annealed contribution due to scattering from thermal density fluctuations.

For wavevectors smaller than the inverse correlation length for density fluctuations ξ, the annealed contribution to the static structure factor is given by a Lorentzian:

$$S(\mathbf{k}) = \frac{S(0)}{1 + \xi^2 q^2} \qquad (1)$$

The long-wavelength ($\mathbf{k} \rightarrow 0$) limit of the structure factor can be expressed as $S(0) = c_0{}^2 k_B T / E_L$ with k_B Boltzmann's constant, T the temperature, c_0 the equilibrium monomer density in a swollen gel, and E_L the longitudinal modulus. As we will show in the following, the physical interpretation of E_L is intimately related to the question whether gels should be considered as solids or as liquids, *on length scales probed by scattering experiments.*

Let us first consider a two-component liquid mixture, for example, a polymer solution. For simplicity, we assume that the mixture is incompressible, i.e., treat the total density (the sum of the densities of the two components) as constant. This means that we only consider variations of the local monomer density c of the polymer component, and the thermodynamic force responsible for these density variations is the osmotic pressure Π (applied through a membrane which is permeable to the solvent but not the polymer). In this case, simple thermodynamic considerations relate the long-wavelength limit of the structure factor to the osmotic compressibility $\partial c/\partial \Pi$ of the polymer solution, and one can readily derive the osmotic *compressiblity sum rule:*[2]

$$S(\mathbf{k} \rightarrow 0) = c_0 k_B T\, \partial c/\partial \Pi \qquad (2)$$

Since the equilibrium osmotic modulus is defined as $E_O^{\mathrm{sol}} = c_0\, \partial \Pi/\partial c$, comparison with eq 1 yields

$$E_L^{\mathrm{sol}} = E_O^{\mathrm{sol}} \qquad (3)$$

and we conclude that, *in liquid mixtures, the osmotic and longitudinal moduli are the same.* The physical content of the compressibility sum rule is very simple—isotropic liquids can only support isotropic stresses (pressure), and therefore their response to isotropic (osmotic) compression and to uniaxial (plane wave) density fluctuations probed by scattering experiments must be controlled by the same modulus.

Now, let us consider a two-component "mixture" which consists of a solid (e.g., a porous medium or a polymer network) permeated by a liquid. Although no ambiguity arises in the case of rigid porous solids which maintain their solid properties (e.g., shear rigidity) on all length scales larger than mesh size,[9] the situation is less clear for "soft" polymer networks. In the latter case it is tempting to assume that swollen gels behave essentially as liquid mixtures and to conclude that the longitudinal and the osmotic moduli are the same. A closer examination of the length scales involved in osmotic (macroscopic) and scattering (since we are interested in the long-wavelength limit, the relevant length scales are of order 10^3–10^4 Å) experiments shows that, with the possible exception of extremely tenuous gels formed at the gelation threshold, these length scales are much larger than the Born–Von Karman length at which shear rigidity is established.[10] On such length scales one must account for a fundamental distinction between solids and liquids, i.e., the existence of long-range elastic fields responsible for the shear rigidity of solids[11] (note that such elastic correlations extend over the whole macroscopic solid and are not related to the "liquidlike" correlation length ξ which is on the order of the mesh size of the network). We therefore conclude that the fundamental description of fluctuations and small deformations of a swollen gel must be that of an isotropic elastic solid, with possible modifications resulting from the coupling to liquidlike degrees of freedom.[12]

An isotropic solid has two elastic moduli: a bulk modulus K which stabilizes the gel against isotropic volume-changing deformations and a shear modulus μ which stabilizes it against shear deformations. A straightforward calculation relates the two moduli to the longitudinal modulus of the gel,[13] $E_L^{\mathrm{gel}} = K + (4/3)\mu$. Notice that, since we assumed that the total network plus solvent system is

---

[†] Yukawa Institute for Theoretical Physics, Kyoto University.
[‡] Bar-Ilan University.
[§] Department of Physics, Kyoto University.

0024-9297/94/2227-0870$04.50/0

incompressible, the only allowed volume changes are those accompanied by a change of the number of solvent molecules within the gel. Therefore, the bulk modulus K is the same as the osmotic modulus of the gel E_0^{gel} and we obtain

$$E_L^{\text{gel}} = E_0^{\text{gel}} + \frac{4}{3}\mu \qquad (4)$$

We emphasize that the above results, eq 3 for liquid mixtures and eq 4 for swollen gels, are general consequences of the thermodynamics of liquid and solid systems, respectively, and are independent of any dynamical assumptions. An important corollary of eq 4 is that, since the shear modulus is positive definite, the longitudinal modulus measured in light scattering and SANS experiments must always be larger than the osmotic modulus obtained by osmotic deswelling or by mechanical experiments *on the same gels*.[14] Although, in principle, all the moduli can be measured independently by different experiments, direct comparison of the results may be difficult because of ambiguities due to unknown prefactors in scattering amplitudes.

An alternative approach was proposed by Tanaka and co-workers, who studied the kinetics of volume changes and dynamics of fluctuations (the latter by dynamic light scattering) near the critical point of the volume phase transition of NIPA gel. They found that the effective diffusion constants obtained from swelling kinetics (D_{kin}) and from dynamic light scattering (D_{co}) vanish at the same temperature at which the gel undergoes a (nearly continuous) volume transition. Since[15] $D_{\text{co}} \propto E_L^{\text{gel}}$ and since, in osmotic equilibrium, $E_0^{\text{gel}} \geq 0$, these results appear to contradict eq 4. A possible way out is to assume that the shear modulus also vanishes at the volume transition point. However, such an assumption has no theoretical basis and, furthermore, direct mechanical measurements of the elastic moduli suggest that the shear modulus remains finite even at the critical point of neutral NIPA gels.[16,17] We propose a different explanation. Note that the argument relating the kinetics of swelling to the osmotic bulk modulus, $D_{\text{kin}} \propto E_0^{\text{gel}}$ is based on linear elasticity[14] and therefore applies only when the volume change is small. This is not the case away from the critical point where volume changes are large and the transition is strictly first order. At the critical point the volume discontinuity becomes small but volume fluctuations diverge and linear theory is again inapplicable. We conclude that nonlinear elasticity and concentration-dependent moduli must be incorporated into the description of the volume transition of gels. Although such a theory was not worked out yet, we expect that close to the critical point the rate corresponding to a truly isotropic volume change (which does not involve the shear modulus) is very small and eventually vanishes as the critical point is approached.[14] This suggests that the observed volume transition does not take place at osmotic equilibrium but rather close to the stability limit ("spinodal") which corresponds to the point where the *longitudinal* modulus vanishes. Further work which combines mechanical and scattering experiments on the same gels, both away from and near volume transitions, is clearly needed to clarify these issues.

Notice that eq 4 does not imply that the longitudinal modulus of a gel has to be larger than the osmotic modulus of a solution of un-cross-linked but otherwise identical polymer chains (measured at the same concentration and temperature as the gel). Such claims were often made in the literature, based on the so-called additivity assumption of the classical theories of gels.[18] According to this assumption, the free energy of the gel is the sum of an elastic term and a contribution from a (Flory–Huggins) free energy of mixing with the solvent, which is assumed to be the same as that for a solution of identical but un-cross-linked chains. Using the classical theory one can show that $E_0^{\text{gel}}(\text{classical}) = E_0^{\text{sol}} - 1/3\mu$ and substitution into eq 4 yields

$$E_L^{\text{gel}}(\text{classical}) = E_0^{\text{sol}} + \mu \qquad (5)$$

Classical theory therefore predicts that $E_L^{\text{gel}} > E_0^{\text{sol}}$ and therefore that the thermal fluctuation contribution to the small-angle scattering from a gel is always smaller than that from a solution, in apparent disagreement with both SANS[19,20] and dynamic light scattering experiments[21] (this behavior is not universal; ref 22 reports $E_L^{\text{gel}}/E_L^{\text{sol}} = 1.5$ in agreement with classical theory, and ref 20 reports that, while this ratio is smaller than unity at low cross-link densities, it exceeds unity at the highest cross-link density investigated). The above discrepancy should not be interpreted as a violation of the thermodynamic relations, eqs 3 and 4, but rather as an indication of the breakdown of the strict form of the classical additivity assumption, according to which the osmotic contribution to the free energy of a gel is the same as the Flory–Huggins free energy of a solution of identical but un-cross-linked polymers. The observation that the osmotic free energy of the gel depends on the state of cross-linking is supported by recent calculations[23] and can explain the anomalies observed in differential swelling experiments.[24–26] It appears plausible that solubility is reduced by the introduction of cross-links, and since, under most conditions (except very close to the critical point), the osmotic modulus is much larger than the shear modulus, the inequality

$$E_L^{\text{gel}} < E_0^{\text{sol}} \qquad (6)$$

may hold for typical polymer–solvent combinations (at the same temperature and concentration). In this case one may expect thermal diffuse scattering from a gel to be stronger than that from a semidilute polymer solution, in particular as one approaches poor solvent conditions. The expectation that the θ point is reached in the gel *before* the solution is supported by the observed scaling of the cooperative diffusion coefficient with concentration in ref 22 and by recent neutron scattering experiments on NIPA solutions and gels which show that thermal scattering from the gel becomes an order of magnitude larger than that from the solution, as the temperature approaches that corresponding to a (continuous) volume phase transition in the gel.[19]

Acknowledgment. We have benefited from helpful discussions with J. Bastide, R. Bruinsma, and M. Shibayama. Y.R. acknowledges a grant from the Israeli Academy of Sciences and Humanities.

References and Notes

(1) Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity*; Pergamon: Oxford, U.K., 1986.
(2) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(3) Mendes, E.; Lindner, P.; Buzier, M.; Boué, F.; Bastide, J. *Phys. Rev. Lett.* **1991**, *66*, 1595 and references therein.
(4) Bastide, J.; Leibler, L.; Prost, J. *Macromolecules* **1990**, *23*, 1821.
(5) Onuki, A. *J. Phys. Fr. II* **1992**, *2*, 45.
(6) Panyukov, S. V. *Sov. Phys. JETP* **1992**, *75*, 347.
(7) Rabin, Y.; Bruinsma, R. *Europhys. Lett.* **1992**, *20*, 79.
(8) Geissler, E.; Horkay, F.; Hecht, A. M. *Phys. Rev. Lett.* **1993**, *71*, 645.
(9) Biot, M. A. *J. Acoust. Soc. Am.* **1956**, *28*, 168.

(10) Alexander, S. In *Physics of Finely Divided Matter*; Boccara, N., Daoud, M., Eds.; Springer: Berlin, 1985.

(11) Ginzburg, V. L.; Sobyanin, A. A.; Levanyuk, A. P. In *Light Scattering and Phase Transitions*; Cummins, H. Z., Levanyuk, A. P., Eds.; North-Holland: Amsterdam, The Netherlands, 1983.

(12) Bruinsma, R.; Rabin, Y. *Phys. Rev. E*, in press.

(13) Tanaka, T.; Hocker, L. O.; Benedek, G. *J. Chem. Phys.* **1973**, *59*, 5151.

(14) Onuki, A. In *Responsive Gels: Volume Transitions*; Dušek, K., Ed.; Springer: Berlin, 1993; Vol. 1.

(15) Tanaka, T.; Sato, E.; Hirokawa, Y.; Hirotsu, S.; Peetermans, J. *Phys. Rev. Lett.* **1985**, *55*, 2455.

(16) Hirotsu, S. *J. Chem. Phys.* **1990**, *94*, 3949.

(17) Li, C.; Hu, Z.; Li, Y. *Phys. Rev. E* **1993**, *48*, 603.

(18) Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 521. James, H. M.; Guth, E. *J. Chem. Phys.* **1943**, *11*, 455.

(19) Shibayama, M.; Tanaka, T.; Han, C. C. *J. Chem. Phys.* **1992**, *97*, 6829.

(20) Horkay, F.; Burchard, W.; Hecht, A.-M.; Geissler, E. *Macromolecules* **1993**, *26*, 3375.

(21) Joosten, J. G. H.; McCarthy, J.; Pusey, P. *Macromolecules* **1991**, *24*, 6690.

(22) Patel, S. K.; Cohen, C. *Macromolecules* **1992**, *25*, 5252.

(23) Freed, K. F.; Pesci, A. I. *Macromolecules* **1989**, *22*, 4048.

(24) Zhao, Y.; Eichinger, B. E. *Macromolecules* **1992**, *25*, 6988.

(25) McKenna, G. B.; Flynn, K. M.; Chen, Y.-H. *Polymer* **1990**, *31*, 1937.

(26) Pekarski, P.; Rabin, Y.; Gottlieb, M., submitted to *J. Phys. Fr. II*.