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## Polymer gels in uniaxial deformation

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**Abstract.** The recent analysis of osmotic pressure in a semi-dilute solution of strongly stretched polymers is used to study the uniaxial stretching of a swollen polymer gel, in a good solvent. The resulting steady-state stress-strain relation complements Daoudi's analysis of the transient deformation of polymer gels.

The transient uniaxial deformation of a swollen polymer gel in a good solvent was studied by Daoudi [1]. He considered a  $c^*$  gel [2, 3] with  $N$  monomers between adjacent cross-links in which the average separation between cross-links is given by the equilibrium dimensions of a coil of  $N$  monomers of size  $b$  each,  $l_0 \approx bN^{3/5}$ , so that the gel forms a close-packed assembly of blobs of size  $l_0$ . When a tensile force  $F$  is applied to the network, it deforms from its equilibrium size  $L_0$  to a stretched size  $L$  and if, furthermore, the deformation is assumed to be affine, each of the chains stretches to a length  $l$  such that the deformation ratio  $\alpha$  is given by  $\alpha = L/L_0 = l/l_0$ . Using Pincus' analysis of the deformation of real chains in good solvents [4], one visualizes each of the segments in the network as a stretched chain of Pincus blobs of size  $\xi_p = l_0/\alpha^{3/2}$  each, and arrives at a force-deformation relation,  $F \approx kT\alpha^{3/2}/l_0$ , where  $k$  is the Boltzmann constant and  $T$  is the temperature [2].

In order to relate the force to the observed stress  $\Sigma$ , one needs to understand how the deformation affects the dimensions of the gel (and of individual chain segments in it) in the plane normal to the direction of stretching. Under steady-state conditions, the transverse dimensions of the stretched gel are determined by the balance between the (expanding) osmotic pressure and the (restoring) elastic force and thus one needs to calculate the osmotic pressure of stretched chains, something that was done only recently by the present authors [5]. This effect was not treated by Daoudi who considered only the transient regime in which the volume of the gel is unchanged by deformation [1]. In this case the equilibrium area per chain ( $l_0^2$ ) has to decrease by a factor  $1/\alpha$  such that the stress-strain relationship becomes [1]  $\Sigma \approx kT\alpha^{5/2}/l_0^3$ . Although, as we show in the following, the steady-state volume of the gel is larger than in equilibrium, the volume change is controlled by the slow process of cooperative diffusion that may take many hours [2] and therefore experiments can be carried out in the transient regime considered by Daoudi.

Consider the long-time behaviour of polymer gels subjected to uniaxial deformation, after the gel density profile had relaxed to its steady-state value. In this limit

the dimensions of the gel normal to the stretching axis and (using the affine assumption), consequently, the separation  $R$  between neighbouring stretched segments, are obtained by equating the osmotic and the elastic forces. Let us focus our attention on a stretched polymer segment between adjacent cross-links. This chain is surrounded by other stretched segments that are nearly parallel to it, such that the average spacing  $R_{\perp}$  between neighbouring chains is determined by the balance between inter-chain excluded-volume repulsions and intra-chain elastic restoring forces. Since for transverse deformations the spring constant of the chain is given by  $kT/\langle R_{\perp}^2 \rangle$  where  $\langle R_{\perp}^2 \rangle^{1/2}$  is the average transverse dimension of the Pincus chains [2] the elastic restoring force is given by

$$F_{el} = \left( \frac{kT}{\langle R_{\perp}^2 \rangle} \right) R_{\perp} = \left( \frac{kT}{n_p \xi_p^2} \right) R_{\perp} \quad (1)$$

where  $n_p = N/(\xi_p/b)^{5/3}$  is the number of blobs per chain. When the stretched chains are separated by an average transverse distance  $R_{\perp}$  the repulsive osmotic force between them is given by [5]

$$F_{osm} = \left( \frac{kT \xi_p^3}{\xi_p R_{\perp}} \right) n_p \quad (2)$$

where we used a mean-field estimate of the excluded-volume interaction energy per blob [5],  $kT \times$  the volume fraction of blobs ( $\xi_p^3/\xi_p R_{\perp}^2$ ). Equating the two forces gives

$$R = \langle R_{\perp}^2 \rangle^{1/2} = l_0 (\xi_p/l_0)^{1/6} \quad (3)$$

in agreement with the intuitive expectation that the steady-state separation between the chains is of the order of their transverse dimensions.

Using the affine assumption for the stress yields

$$F = \Sigma R_{\perp}^2 \quad (4)$$

where the applied force  $F$  equals to the difference between the Pincus force  $kT\alpha^{3/2}/l_0$  and the osmotic force  $kT\alpha^{1/4}/l_0$ . The latter force (not considered by Daoudi) is much smaller than the Pincus force (for  $\alpha \gg 1$ ) and will be neglected in the following. After some algebra we obtain the stress-strain relation

$$\Sigma = kT\alpha^2/l_0^3. \quad (5)$$

When the gel is subjected to a fixed strain, the stress is expected to exhibit a transient overshoot,  $\Sigma(t \rightarrow 0) \sim \alpha^{5/2}$ , followed by a slow decay to a steady-state plateau,  $\Sigma(t \rightarrow \infty) \sim \alpha^2$ . During the stretching, the (transverse) area of the gel shrinks from  $L_0^2$  to  $L_0^2/\alpha$  and then expands to  $L_0^2/\alpha^{1/2}$ . The volume of the gel does not change at first and then slowly increases [6] from  $L_0^3$  to a steady-state value  $\alpha^{1/2}L_0^3$ . These phenomena are expected to take place at large uniaxial deformations of the gel,  $\alpha \gg 1$ . For inter-cross-link spacings of 500 Å this implies stresses much larger than  $\Sigma^* = kT/l_0^3 \approx 500 \text{ dyn cm}^{-2}$ . Although the conditions under which the present theory applies (large deformation of  $c^*$  gels) may be difficult to achieve in practice, we hope that our results will stimulate experimental work in this direction.

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