Frustrated Spring-network Model for Crosslinked Polymer Surfaces

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Abstract. We present a simplified model to study the surface structure of a crosslinked polymer gel. The model consists of a two-dimensional spring network on a triangular lattice. The nodes represent the crosslinkers, and the equilibrium length of the harmonic springs between nodes is associated with the random length of a polymer chain between crosslinkers. Our preliminary results show that this model qualitatively reproduces some characteristics of surfaces of polyacrylamide gels into which holes are introduced through templating with surfactant micelles, recently observed by Atomic Force Microscopy. There is a length scale above which the surface width reaches a saturation value. This saturation value appears to be independent of the system size but changes significantly when holes are introduced in the system.

1 Introduction

Crosslinked polymer gels are widely used in electrophoresis and chromatography. Their excellent ability to separate macromolecules is largely due to their wide range of pore sizes. Recently, the separation properties of polyacrylamide gels have been further enhanced by the introduction of a controlled density of holes in the polymer matrix. The holes are produced by templating the gels with uniformly sized surfactant micelles during polymerization, which are subsequently leached out in water [1]. The holes significantly change both the optical properties of the gel and the structure of the free gel surface.

The dependence of the surface structure on the hole concentration was recently investigated by Atomic Force Microscopy (AFM) and scaling analysis of the surface height on length scales between 1 nm and 20 μm [2]. The gel surfaces were observed to be generally self-affine on short length scales, with roughness (Hurst) exponents [3,4] on the order of 0.8–1.0, crossing over to a scale-independent rms surface width for length scales larger than a crossover value. Both the crossover length and the saturation value of the rms surface width increased significantly with the hole concentration. In particular, changing the micelle concentration between 0% and 40% by weight changed the crossover length from approximately 300 nm to 600 nm and the saturation value of the rms surface width from roughly 1 nm to 100 nm.

Here we present preliminary results from a project to construct and study a two-dimensional toy model of a crosslinked polymer to attempt to reproduce the observed surface structure and its dependence on the concentration of holes.

2 Model and Results

While detailed kinetic models for the polymerization of crosslinked gels have been constructed [5], they are very computationally intensive. We therefore instead developed a two-dimensional random, elastic network model that mimics the structure of the crosslinked polymer and its free surface in a semi-quantitative fashion without being too computationally demanding. This approach enables us to generate multiple realizations of large systems, thus reducing finite-size effects and statistical uncertainties.

The model is built from a regular, triangular lattice of unit lattice constant, whose nodes represent the crosslinking units of the gel. On the bonds are placed harmonic springs whose equilibrium lengths l_0 are assumed to be proportional to the square root of an exponentially distributed number of monomers between crosslinking units. Thus l_0 corresponds to the end-to-end distance of a polymer in the random-coil collapsed phase [6]. The probability density for l_0 is thus

$$P(l_0) = 2\gamma l_0 \exp\left(-\gamma l_0^2\right), \tag{1}$$

where γ is proportional to the inverse of the average number of monomers between crosslinkers. The average equilibrium length of a spring is then $\langle l_0 \rangle = \sqrt{\pi/\gamma}/2$. We also require that springs with a small l_0 should be stiffer than longer springs, which we enforce through a spring constant proportional to l_0^{-1}. The resulting probability density for the (dimensionless) force F, exerted by a spring of actual length l, then becomes

$$P(F|l) = \frac{2\gamma l^2}{(1-F)^3} \exp\left[-\gamma \left(\frac{l}{1-F}\right)^2\right], \tag{2}$$

yielding the average force exerted by a spring of length l as

$$\langle F|l \rangle = (1 - l\sqrt{\gamma\pi}) \ . \tag{3}$$

We seek a model in which the uniform reference configuration represented by the regular triangular lattice of unit lattice constant is *locally*, but not *globally* stressed. Thus, the average force exerted by a spring of unit length should vanish. By (3) this requires $\gamma = 1/\pi$. Using this value of γ, springs with equilibrium lengths l_0 drawn from $P(l_0)$ are placed randomly on all the bonds. The local stresses are then relaxed by a steepest-descent calculation until a (locally stable) configuration is reached. Periodic boundary conditions are imposed in the horizontal direction. The bottom layer of nodes is kept fixed

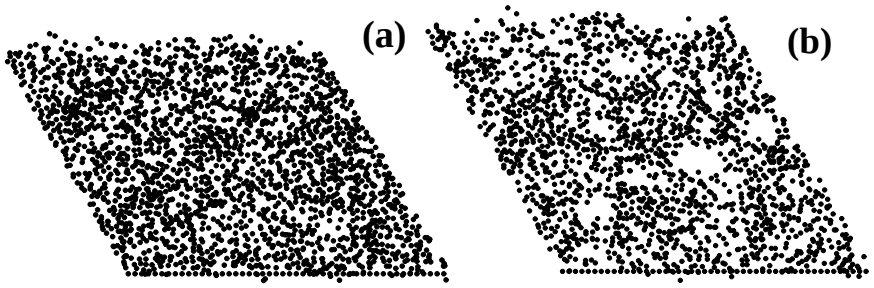

Fig. 1. Bulk configurations of a 48×48 system, shown after relaxation. The nodes, which represent crosslinkers, are shown as dots. For clarity the bonds, which represent polymer chains, are not shown. The inhomogeneity of the crosslinker distribution in the bulk is visible. (**a**) Without holes. (**b**) With 18% vacant nodes. Even for this small system the different roughness of the surfaces is apparent to the eye

and the top surface is allowed to relax freely. Holes are created by eliminating randomly chosen nodes and their connecting springs. After relaxation the average density of the system (in nodes per volume) remains constant in the bulk, while a slight contraction of the surface, limited to approximately the top 120 layers, is observed. A relaxed system of size 48×48 is shown in Fig. 1 as an illustration, both without (a) and with (b) holes. We note that this system is too small to allow for an accurate numerical analysis. Nevertheless, inhomogeneities in the crosslinker distribution that are also seen in larger systems are evident to the eye, even in the case where there are no vacancies [Fig. 1(a)]. Such inhomogeneities are characteristic of polyacryalmide gels [7] and have been related to a freezing-in of the topological structure of the system [8,9].

A simple way to analyze the surface roughness is to consider the rms surface width over a box of length L,

$$w(L) = \sqrt{\langle y^2 \rangle_L - \langle y \rangle_L^2}\,, \tag{4}$$

as a function of L. For a self-affine surface

$$w(L) \sim L^{\alpha}, \tag{5}$$

where α is the Hurst exponent (here identical to the roughness exponent [4]). For L larger than a crossover length $L_{\times}$, $w(L)$ saturates to an L-independent value, $w_{\rm sat}$. In contrast to standard surface-growth problems [3,4], $w_{\rm sat}$ does *not* seem to depend on the system size, but is an intrinsic system property. In Fig. 2 we show $w(L)$ vs. L on a log-log scale for systems of different sizes with no holes [Fig. 2(a)], and for a 256×256 system with no holes and with holes created by an 18% concentration of vacant nodes [Fig. 2(b)]. From these preliminary results we are not able to determine the behavior of the system on small length scales; the system may be self-affine, but we do not yet have sufficient data to calculate a roughness exponent.

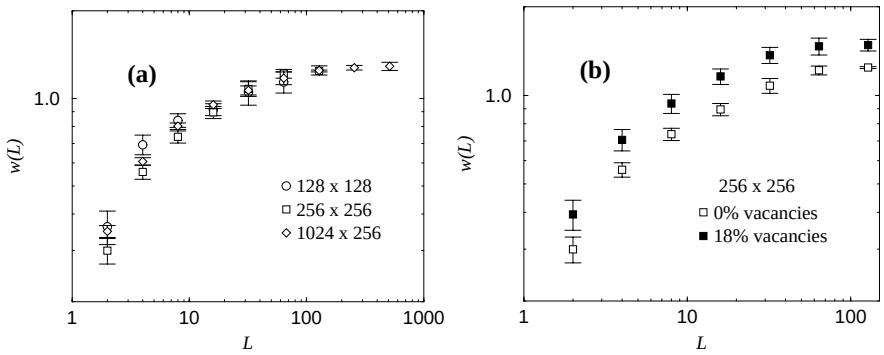

Fig. 2. Average values of the rms surface width over boxes of length L, w_L, shown on a log-log scale vs. L. The vertical scale runs from 0.2 to 2.0. (**a**) For systems of size 128×128, 256×256 and 1024×256 without holes. The crossover length $L_\times$ and the saturation width $w_{\rm sat}$ are both seen to be independent of the system size. (**b**) For a system of size 256×256, with no holes and with 18% of the nodes missing. The difference in the saturation width due to the presence of the holes is evident

3 Conclusion

Our preliminary results show that our spring-network model can qualitatively reproduce some aspects of the behavior of templated gel surfaces observed by AFM. There is a length scale above which the rms width of the surface reaches a saturation value. This saturation value appears to be independent of the system size, but it depends on the concentration of holes in the system. The surface generated by the model may be self-affine on small length scales. Further work on larger systems is needed in order to clarify this point and measure the roughness exponent α if the surface is self-affine.

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