Surface scaling analysis of hydrogels: From multiaffine to self-affine scaling

G.M. Buendía¹, S.J. Mitchell², P.A. Rikvold³
¹Departamento de Física, Universidad Simón Bolívar, Caracas 1080, Venezuela
²Shuit Institute for Catalysis and Department of Chemistry and Chemical Engineering, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
³Center for Materials Research and Technology, School of Computational Science and Information Technology, and Department of Physics, Florida State University, Tallahassee, Florida 32306-4350, USA

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Abstract

We show that smoothing of multiaffine surfaces that are generated by simulating a crosslinked polymer gel by a frustrated, triangular network of springs of random equilibrium lengths [G.M. Buendía, S.J. Mitchell, P.A. Rikvold, Phys. Rev. E 66 (2002) 046119] changes the scaling behavior of the surfaces such that they become self-affine. The self-affine behavior is consistent with recent atomic force microscopy (AFM) studies of the surface structure of crosslinked polymer gels into which voids are introduced through templating by surfactant micelles [M. Chakrapani, S.J. Mitchell, D.H. Van Winkle, P.A. Rikvold, J. Colloid Interface Sci., in press]. The smoothing process mimics the effect of the AFM tip that tends to flatten the soft gel surfaces. Both the experimental and the simulated surfaces have a non-trivial scaling behavior on small length scales, with a crossover to scale-independent behavior on large scales.

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1 Introduction

In a recent study [1] we proposed a frustrated spring-network model to simulate the surface structures of crosslinked polymer gels into which voids are introduced
through templating by surfactant micelles. Experimentally, templated polyacrylamide gels are created by mixing acrylamide with a crosslinker in the presence of a surfactant [2]. The resultant gels have a wide range of pore sizes, making them ideal materials for macromolecular separation [3]. The crosslinking process introduces inhomogeneities in the spatial density of the gel that affect its surface configuration. Our results show that the surfaces generated by the spring-network model have a nontrivial, multiaffine scaling behavior at small length scales, with a crossover to scale-independent behavior on large scales.

At small length scales we found that the $q$th order increment correlation function has a power-law behavior, with $q$-dependent exponents that change with the vacancy concentration. However, experimental surfaces of surfactant-templated hydrogels studied by atomic force microscopy (AFM) [4] show $q$-independent self-affine scaling at length scales below the crossover length. In Ref. [1] we discussed the possibility that the multiaffine behavior was due to a finite density of vertical discontinuities due to overhangs in the simulated surfaces. Later work showed analytically and numerically that when vertical discontinuities are introduced into a self-affine surface, it becomes multiaffine [5]. Here we extend this study to hydrogel surfaces, and we show that smoothing the simulated surfaces by convoluting them with a Gaussian changes the scaling behavior from multiaffine to self-affine, in agreement with the experimental AFM results. The smoothing process mimics the effect of the measurement process of an AFM tip interacting with the soft substrate.

2 The frustrated spring-network model

The model, described in detail in Ref. [1], consists of a two-dimensional triangular network of nodes interconnected by massless harmonic springs. The nodes represent the crosslinkers, and the springs correspond to the polymer chains. We impose periodic boundary conditions in the horizontal direction, while the top nodes are free to move in two dimensions. The bottom nodes are fixed, corresponding to bonding to a rigid substrate.

We assume that each spring corresponds to a collapsed polymer chain with equilibrium end-to-end length $l_{0i}$, which is randomly chosen with probability density

$$P(l_{0i}) = 2\gamma l_{0i} \exp(-\gamma l_{0i}^2)$$

Thus, $l_{0i}$ is proportional to the square root of an exponentially distributed number of monomers between crosslinkers [6]. The constant $\gamma$ is proportional to the inverse of the average number of monomers between crosslinkers. Consistent with the picture of a random-coil collapsed polymer chain, we require that the elastic constant of each spring, $k_i$, be proportional to its equilibrium length, $k_i = 1/l_{0i}$ in dimensionless units [7].

For each statistical realization of the system, the equilibrium spring lengths are chosen independently according to Eq. (1). In the initial network configuration, all springs are placed on the bonds of a regular triangular lattice of unit lattice constant, such that all springs are stretched or compressed to unit length, $l_i = 1$. This initial
configuration is highly stressed. However, by choosing the value of $\gamma$ such that the average force exerted by each spring is zero, we ensure that the initial configuration is not globally stressed. From the initial configuration, the system is relaxed to one of its many local energy minima by a limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) quasi-Newton minimization algorithm [8], and by repeating the calculations for several different realizations of the equilibrium spring lengths we verified that the statistical properties of the different relaxed configurations are essentially the same.

Spring networks of $L_x \times L_y = 1024 \times 768$ nodes were generated, and voids were introduced by randomly removing nodes and the springs connected to them. The Hoshen-Kopelman algorithm [9] was applied to eliminate clusters that were not connected to the fixed substrate, thus mimicking the removal of non-bonded material which is washed away during the experimental preparation.

3 Calculations

The one-dimensional surfaces are defined as the set of surface heights, $h(x_i)$, at equally spaced discrete horizontal points, $x_i$. The surface height at $x_i$, $h(x_i)$, is taken as the largest vertical distance, measured from the bottom, of the intersections of the springs with a vertical line at $x_i$, where each spring is represented by a straight line segment between the connected nodes. This definition of the surface is described in more detail in Ref. [1].

The $q$th order generalized increment correlation function is defined as [10]

$$C_q(r) = \langle |h(x_0 + r) - h(x_0)|^q \rangle$$

For many surfaces, $C_q$ displays a power-law behavior, such that

$$C_q(r) \propto r^{qH_q}$$

where $H_q$ is the generalized Hurst exponent [10] [11]. For self-affine surfaces, the scaling behavior is independent of $q$, $H_q = H$, but for multi-affine surfaces, there is an infinite hierarchy of scaling exponents, such that $H_q$ depends continuously on $q$, at least for some range of $q$ values and length scales [12].

Very often surfaces present a mixed behavior. For length scales smaller than some crossover, $r < l_x$, $C_q$ displays a non-trivial scaling behavior, while at length scales larger than this crossover, $r > l_x$, $C_q$ is constant, $C_q(x) \approx C_q^{\text{sat}}$. In our previous work [1] it was shown that the simulated gel surfaces are multi-affine, and the scaling exponents, crossover length scales, and saturation values of the increment correlation function are strongly dependent on the void concentration. Despite the fact that the experimental surfaces seem to have a similar dependence on the void concentration, one major difference between the simulated and experimental surfaces remains: The experimentally measured surfaces are clearly self-affine on short length scales [2] [4], while the simulated surfaces are clearly multi-affine [1].

Recent work [5] indicates that vertical discontinuities are one important source of multi-affinity, and the surfaces generated by our model certainly have many vertical
4 Conclusions

In this paper we have shown that surfaces generated by a frustrated spring-network model can reproduce several aspects of the scaling behavior of surfaces of surfactant-templated polyacrylamide gels, as observed in recent AFM experiments [4]. Both real and simulated surfaces show a nontrivial scaling behavior characterized by a...
Figure 2: The $q$th root of $C_q(r)$ from the spring-network surfaces for $q = 0.5$ to $q = 4.0$ in steps of 0.5. For graphical simplicity, the $q$ labels have been omitted, but $C_i(r) > C_j(r)$, when $i > j$. The surfaces are averaged over 8, 8, and 10 independent realizations of the equilibrium spring lengths for the networks with 0%, 40%, and 49% vacancies, respectively. The linear regions of the plot indicate power-law scaling, and for the original simulated surfaces, the different power-law exponents (slopes in the log-log plots) indicate $q$-dependent multiaffine scaling. After smoothing, the power-law scaling at small length scales is self-affine (parallel lines in the log-log plots) with $H_q = 1$ for all $q$. 
Figure 3: $H_q$ vs. $1/q$ for the spring-network surfaces. Open symbols indicate the original, multiaffine surfaces, while corresponding filled symbols indicate the smoothed, self-affine surfaces. As expected, $H_q = 1.0$ for all of the smoothed surfaces. The observed multiaffine scaling of the original surfaces is consistent with the behavior caused by vertical discontinuities as expected from Ref. [5]. The data are averaged over 8 independent realizations of the equilibrium spring lengths for 0% to 47% vacancies, 10 realizations for 49% vacancies, and 14 realizations for 49.5% vacancies.

The power-law form of the increment correlation function at small and intermediate length scales. At larger length scales the increment correlation function reaches a saturation value. This large-scale behavior reflects the average network structure, while the small-scale behavior is due to microscopic density fluctuations. Below some crossover length, the experimental surfaces are self-affine while the original simulated surfaces are multiaffine. We show that after smoothing by convolution with a narrow Gaussian, which eliminates vertical discontinuities, the simulated surfaces become self-affine. Such smoothing mimics the effect of passing a weakly interacting AFM tip over the soft hydrogel surfaces. The large-scale behavior is not affected by the smoothing process.

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