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Entropic elasticity of a regular fractal

Edgardo Duering and Yacov Kantor
School of Physics and Astronomy, Tel Aviv University, Ramat-Aviv, Tel Aviv 69978, Israel
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We apply the Monte Carlo method to investigate the *entropic* elasticity of a model structure with a regular fractal connectivity. We find deviations from Flory theory and from the simple scaling predictions used in polymer physics: Unlike linear polymers, the system here maintains its shape on large length scales, and its relative fluctuations decrease with increasing system size, while the behavior of the elastic constants resembles that of energy-dominated models.

In recent years there has been a renewed interest in the elastic properties of *inhomogeneous* systems. In such systems one can usually identify a geometrical correlation length ξ, above which the material can be treated as homogeneous. Frequently at lengths $L<\xi$, the geometrical properties of the system can be characterized by a fractal dimension[1] d_f, which relates the mass N of a fractal object N to its linear size L: $N\sim L^{d_f}$. In that regime, the physical properties of a fractal have a power-law dependence on L. In particular the mean two-point resistance increases as L^{ζ_r}. Similar behavior but with different exponents has been found in several models of elasticity.[2-5] Elastic properties for $L>\xi$ are inferred from the elastic properties in the fractal regime by assuming a smooth crossover from the fractal to the homogeneous regime. The elastic stiffness tensor C_{ijkl} of a *homogeneous* solid is simply related to the shape and volume dependence of its free energy F:[6] $C_{ijkl}=(1/V)\partial^2 F/\partial\varepsilon_{ij}\partial\varepsilon_{kl}$, where ε_{ij} is the strain tensor, and V is the volume of the system. In general, at finite temperature T, both the energy $\mathcal{U}$ and the entropy $\mathcal{S}$ contribute to the shape dependence of $F=\mathcal{U}-T\mathcal{S}$. While in most solids the elasticity is determined by the shape and volume dependence of $\mathcal{U}$, in polymeric structures, such as rubbers or gels[7] it is dominated by the entropy: The distortion of a network reduces the available phase space thus decreasing the entropy of the system.[8] Linear and branched polymers are examples of entropy-dominated tenuous structures. They do not have a "ground-state shape," and can be defined only by their *connectivity,* while the shape fluctuations in the fractal regime are of order unity. The radius of gyration (rms size) of the system R_g can usually be related to its *internal* linear size L (in the case of a linear polymer, L is the number of monomers, while in the case of a polymeric surface, L is the linear size of a stretched surface) by a power law: $R_g\sim L^{\nu}$. In such a situation one cannot use a regular stiffness tensor. However, the scaling $k\sim L^{-\zeta_e}$ of a typical force constant k can be easily determined: Since the typical fluctuation δ satisfies[9] $k\delta^2\approx k_BT$, and δ is of order R_g, the force constant[10] $k\approx k_BT/R^2\sim L^{-2\nu}$. Thus, the elasticity exponent $\zeta_e=2\nu$ for polymeric structures. In this Rapid Communication, we consider a particular type of deterministic fractal, which has the connectivity of Sierpiński gasket. We show that the relative shape fluctuations of the structure decrease with increasing L and its $\nu=1$, while the elastic constants exhibit an L dependence different from the aforementioned prediction. These results contradict the standard scaling assumptions for polymeric networks, and provide an example of a noncompact system which is able to maintain its shape at finite temperature on arbitrary length scales.

The success of the scaling theory in polymer physics rests on detailed investigation of linear polymers.[7] We attempted to depart as far as possible from the linear polymer case, and investigated a system which has the *connectivity* of Sierpiński gasket. This high-connectivity deterministic fractal is constructed from a triangle, which is subdivided into four triangles by lines connecting the midpoints of its edges, followed by removal of a central triangle and inflation of the entire structure by a factor of 2. The procedure is repeatedly applied to each of the remaining triangles. For such a gasket[11] $d_f=\ln 3/\ln 2\approx 1.585$ and $\tilde{\zeta}_r=\ln\frac{5}{3}/\ln 2\approx 0.737$. This model has already been used to investigate the *energetic* elasticity.[4,5]

Our two-dimensional model system is described by the Hamiltonian

$$\frac{H}{k_BT}=\sum_{\langle i,j\rangle_{nn}}V_{\rm att}(|\mathbf{r}_i-\mathbf{r}_j|)+\sum_{\{i,j\}}V_{\rm rep}(|\mathbf{r}_i-\mathbf{r}_j|), \quad (1)$$

where $\mathbf{r}_i$ is the positions of ith atom. The attractive potential $V_{\rm att}$ acts only between pairs $\langle i,j\rangle$ of atoms, which are nearest neighbors on a regular Sierpiński gasket, thus ensuring the *connectivity* (but *not the shape*) of the gasket. We chose $V_{\rm att}(r)=0$, for $r<b$, and ∞ otherwise. (This type of "tethering potential" has been previously used to investigate self-avoiding surfaces.[12]) The excluded-volume (or self-avoiding, or steric) interaction was implemented by a hard-core repulsive potential ($V_{\rm rep}=0$, for $r>a$, and ∞ otherwise), which acts between *any pair* $\{i,j\}$ of atoms. Neither $V_{\rm att}$ nor $V_{\rm rep}$ have an energy scale: All permitted configurations have a vanishing potential energy. Thus, the physical properties of the system are determined by the entropy, and the force constants are strictly proportional to T. We chose $b=3a$, which permits an atom to penetrate through a bond connecting a pair of neighboring atoms.

The configuration space of the structure has been sampled using the Monte Carlo (MC) method[13] which consisted of randomly picking an atom and attempting to displace it by $s=0.5a$ in a randomly chosen direction. During a "MC time step" on the average one attempt was

made to move every atom once. We monitored the time-time correlation functions of R_g and various strains, and the rotational motion of the entire structure. In a regular polymeric structure one expects[10] the maximal relaxation time of "vibrational" (internal) mode (such as fluctuations of R_g) to be comparable with the time it takes the structure to diffuse a distance equal to R_g or to rotate by an appreciable angle. The latter two times can be shown to be of order $\tau_R = R_g^2 N/s^2 \sim L^{2\nu+d_f}/s^2$. We found[14] that, in large gaskets, the internal modes relax by many orders of magnitude faster than τ_R. However, to avoid a doubt regarding the statistical independence of configurations, and to ensure sufficiently accurate averages, the total simulation time significantly exceeded τ_R. We investigated systems whose connectivity was determined by n times iterated Sierpiński gasket for $n=0,1,\ldots,5$. The structure contains $N=(3^{n+1}+3)/2$ atoms, and its internal linear size is *defined* as $L=2^n$. Thus the largest structure (depicted in Fig. 1) consisted of 366 atoms. The considered size was limited by the required CPU times which increase as $\tau_R N \sim L^{2(\nu+d_f)} \approx L^{5.2}$ and for $n=5$ required several months of CPU on a Sun 3/140 minicomputer. For each n we analyzed the physical properties of the gasket on the internal length scales $l=2^{n'}$ with $0 \le n' \le n$.

It is believed that on a sufficiently long length scale a tenuous network without self-avoidance can be correctly described by a network of harmonic springs which have a vanishing equilibrium length. It can be shown[15,16] that the squared radius of gyration R_{g0}^2 of such a polymeric network is proportional to the mean resistance of a resistor network, which has the same topology as the polymeric network. Therefore, in the absence of the self-avoidance in our model system we should expect $R_{g0} \sim L^{\nu_0}$, with $\nu_0 = \tilde{\zeta}_r/2 \approx 0.368$. To verify this behavior we equilibrated

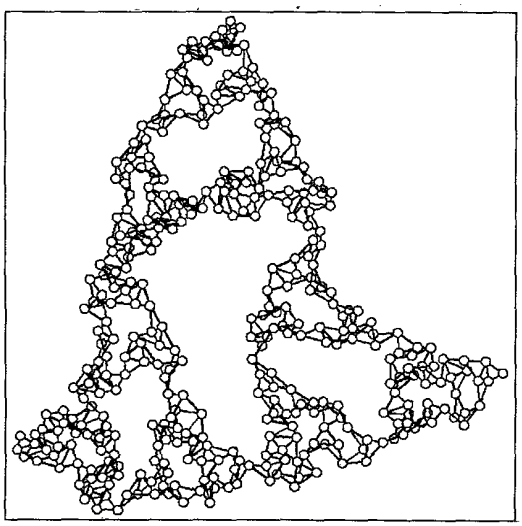

FIG. 1. Typical equilibrium configuration of a polymer which has the connectivity of Sierpiński gasket, which has been obtained after $n=5$ iterations of the original triangle. The circles represent the extent of the hard-core repulsive potential, while the lines indicate the neighboring pairs of atoms between which the attractive ("string") potential acts.

a modified version of our model in which V_{rep} was restricted to act only between the nearest neighbors of the network. We found an excellent agreement between the predicted power law and the measured L dependence of R_{g0} of the system already for $n \sim 3$.

Excluded volume interactions cause an expansion of the system (compared with the case without self-avoidance) and an increase in ν. From dimensional analysis one finds that the self-avoidance becomes irrelevant when the structure is embedded in space dimension[15] $d > d_c \equiv 4d_f/\tilde{\zeta}_r$. For a structure with the connectivity of a two-dimensional Sierpiński gasket the upper critical dimension $d_c \approx 8.6$. For $d < d_c$ we can approximate the free energy F by a Flory-type expression:[17]

$$\frac{F}{k_B T} = \left(\frac{R_g}{R_{g0}}\right)^2 + v\left(\frac{N}{R_g^d}\right)^2 R_g^d , \qquad (2)$$

where we omit the dimensionless prefactors of order unity. The first term on the right-hand side of (2) is the elastic (entropic) free energy of a network (R_{g0} is the radius of gyration of the same network without self-avoidance). The second term is an estimate of the repulsive interaction energy [the squared density of the monomers $(N/R_g^d)^2$ is a mean-field-type estimate of the number of pairs of monomers coming into close contact with each other in a unit volume]. By minimizing (2), we find $R_g \sim L^{\nu_F}$, with $\nu_F = (\tilde{\zeta}_r + 2d_f)/(d+2)$. For Sierpiński gasket in $d=2$, $\nu_F = 0.977$. Notice that for $d < d_k \equiv \tilde{\zeta}_r + 2d_f - 2$, we have $\nu_F > 1$. In general, the definition of the internal size L is somewhat arbitrary (the value of ν depends on that definition) and ν can exceed unity. However, with the particular definition used for our model we must have $\nu \le 1$, and the Flory-type approximation must break down at $d_k \approx 1.907$. Notice that d_k is *not* analogous to the lower critical dimension of a regular manifold since the object does not become compact at that dimension of the embedding space. We should also keep in mind that the expression for d_k has been obtained within an approximate treatment.

In the MC simulations we measured R_g for a sequence of gasket sizes L. For small L the effective value of ν is somewhat smaller than unity, but it increases with increasing L and tends towards $\nu = 1.002 \pm 0.005$, leaving the Flory estimate outside the error bars. Since $\nu \le 1$, our result suggests that $\nu = 1$ *exactly*. This conclusion also follows naturally from a simple inspection of Fig. 1: We notice that on short length scales the structure is quite featureless. However, on larger length scales the "regular" shape of the gasket becomes apparent. This behavior, resembling homogeneous structure, indicates that $\nu = 1$.

The "shape stability" permits introduction of a regular elastic compliance tensor S_{ijkl}, and its MC measurement from the strain fluctuations:[18] $S_{ijkl} = (\mathcal{A}/k_B T)\,\langle \varepsilon_{ij}\varepsilon_{kl}\rangle$, where $\mathcal{A}$ is the area of the system. The thermally induced strains ε_{ij} on length scale $l=2^{n'}$ in a gasket of size $L=2^n$ have been defined by the deviations from the average shape of a parallelogram constructed from two vectors joining one corner atom of a selected ("triangular") substrate of size l to the other two corners of the substructure, while $\mathcal{A}$ was defined as the average area of the parallelo-

gram. One side of the parallelogram has been defined as $i=1$ direction, thus attaching the reference frame to the object, which may rotate in the space. The results have been averaged over substructures and time. All nonvanishing elements of S_{ijkl} had the same l dependence, and were consistent with the (expected) isotropic symmetry, thus reducing the results to two independent constants with the same scaling properties. For fixed l we found a weak dependence on L. Figure 2 depicts the l dependence of the shear modulus μ. Each data point is a result of extrapolation to $L \rightarrow \infty$. The slope of the graph produces an estimate of the entropic elasticity exponent $\tilde{\zeta}_e = 0.90 \pm 0.15$, which is close to the value 1 expected in the energetic elasticity models of the gasket[4,5] with central forces (with or without bending forces), and somewhat exceeds the value 0.737 which would follow from a scalar elasticity model.[5] The result is, obviously, inconsistent with $\tilde{\zeta}_e = 2\nu = 2$, which would be expected in a polymeric system.

The emergence of the "energetic value" of $\tilde{\zeta}_e$ in a purely entropic model is not surprising once we accept the fact that the excluded volume interactions are able to "stabilize" the structure on a particular length scale, at which the system can already be described by an effective Hamiltonian, which has a structure of energetic elasticity models. One can solve such Hamiltonian in harmonic, i.e., small fluctuation, approximation and show that in the case of Sierpiński gasket the relative temperature-induced fluctuations decay with increasing gasket size, thus rendering the solution self-consistent.

Our results demonstrate a case of high-connectivity polymer, which deviates from the simple scaling rules of polymer physics. It also implies the modification of the properties of melts and networks, which, below their correlation length, have a similar structure. It would be useful to find a general criterion for the conditions under which the excluded volume effects are able to stabilize the shape of the structure. We believe that for the sufficiently high space dimension the "regular" polymeric behavior will be restored. In that sense, our simulation was performed below the "true" value of d_k, which was introduced only as a result of a calculation related to Flory-type approximation. One should keep in mind that the "true" value of d_k may depend on additional features of the connectivity of the fractal, which played no role in the derivation of that approximation. To determine those features, it would be useful to investigate the entropy-dominated behavior of several additional models.

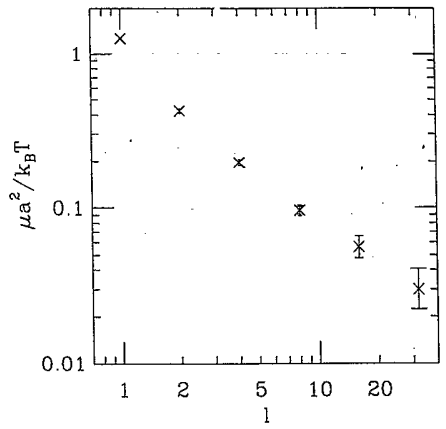

FIG. 2. Logarithmic plot of the (dimensionless) shear modulus as a function of the *internal* length scale l. Each data point has been obtained by extrapolating the measured constants for a *fixed* internal distance to an infinite gasket size. The error bars represent the uncertainty in the extrapolation.

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