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Entropic elasticity of tethered solids

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Elastic properties of a variety of structures, such as polymers, noble element solids, and solids with very unharmonic interatomic potentials, are dominated by the shape and volume dependence of the entropy. The suggested tethered solid model consists of a periodic array of atoms that interact via potentials with infinite barriers. The potential energy of the system vanishes identically, and its properties are determined by the entropy. Elastic moduli of the solid are strictly proportional to the temperature. The model is used to test some approximate approaches to the problem of entropic elasticity, as well as a "toy example" of emergence of a *harmonic* response from unharmonic forces.

I. INTRODUCTION

Elastic properties of solids are determined by the shape and volume dependence of their free energy F.[1] In general, at finite temperature T both the energy $\mathcal{U}$ and the entropy $\mathcal{S}$ contribute to the shape dependence of $F=\mathcal{U}-T\mathcal{S}$. In homogeneous solids, one can usually calculate the elastic constants from purely energetic considerations (assuming that the interatomic potentials are known). However, in certain cases, such as noble-element solids[2] (frequently modeled as solids of "rigid spheres"[3]), the shape dependence of the entropy plays a major role. The elastic compliance tensor S_{ijkl} can be related to the strain fluctuations $\delta\epsilon_{ij}$ in a finite volume A via[4]

$$S_{ijkl}=\frac{A}{k_BT}\langle \delta\epsilon_{ij}\delta\epsilon_{kl}\rangle \ , \tag{1.1}$$

where $\langle\ \rangle$ denotes the thermal average. In the energy-dominated systems $\delta\epsilon_{ij}$ depends on the temperature and is usually small even on the atomic scale, while in the entropy-dominated systems it is temperature independent and may be of order unity.

While the difference between the "energetic" and the "entropic" elasticity is rather technical in homogeneous solids, very different theoretical approaches are required, when tenuous structures, such as linear and branched polymers, rubbers,[5] or tethered (polymerized) surfaces,[6,7] are considered. Theory of elasticity of polymers and polymeric networks is a well-established subject.[5] It provides a typical example of the entropic elasticity. The physical properties of, say, branched polymers are determined solely from the connectivity of the monomers and the excluded volume interactions (i.e., repulsion between the monomers). Thus the calculations are reduced to the measurement of the available phase space under the specified geometrical restrictions. Beyond a short persistence length, one can disregard the particulars of the intermonomer potentials, the concept of the "shape of the system in a ground state" loses its meaning, while the shape fluctuations of the entire structure become of order unity. The elastic response of a stretched polymer is determined by the reduction of the phase-space volume (reduction of the entropy $\mathcal{S}$), and the force constant is proportional to T.

The most important entropy-dominated systems are not analytically solvable. Therefore, it is useful to have a simple solvable "toy model," which will serve as a test system for various approximations. The main feature of the tethered solid described in Sec. II is the vanishing potential-energy part of the free energy, which is achieved using infinite potential barriers. Such a model has been used in the numerical simulations of sheet polymers (tethered surfaces[7,6]), as well as in continuum[8] and discrete[9] simulations of linear polymers. These simulations, however, considered a more complicated case, such as[7,6] a *two*-dimensional tethered surface embedded in *three* dimensions, while in this paper I consider a simpler case, where the dimensionalities of the solid and of the space coincide.

From the pedagogical point of view, one may think of the model as a simple demonstration of several quite nonintuitive thermodynamic phenomena, such as the emergence of the *harmonic* response from unharmonic potentials, temperature dependence of elastic constants, and the "symmetry-breaking" effect of the excluded volume interactions. The tethered solid is an extreme opposite to the "regular" ideal solid with purely harmonic interatomic potentials. While some details of the model are quite unrealistic, it is simple and rich enough to demonstrate several entropy-dominated phenomena.

In the following sections the model is described and analyzed in one and two dimensions. Two simple approximate approaches are tested versus an exact solution and results of numerical simulations.

II. TETHERED SOLID MODEL

Consider a d-dimensional periodic array of atoms, positioned at $\{\mathbf{r}_i\}$, embedded in space of the same dimension. Such an array defines the connectivity of the solid. Atoms of the array repel each others hard-core repulsion, i.e., for *any* pair of atoms i and j the repulsive potential is

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$$V_r(r_{ij})=\begin{cases}\infty & \text{if } r_{ij}<a,\\ 0 & \text{otherwise,}\end{cases} \tag{2.1}$$

where $r_{ij}\equiv|\mathbf{r}_i-\mathbf{r}_j|$. The nearest-neighbor (NN) atoms of the array are tethered by a string, i.e., the distance between them cannot exceed b. Thus the attractive part of the potential is

$$V_a(r_{ij})=\begin{cases}\infty \text{ if } r_{ij}>b \text{ and if } i \text{ and } j \text{ are NN}\\ 0 \text{ otherwise.}\end{cases} \tag{2.2}$$

The total NN interaction V_a+V_r is a square-well potential, which can be thought of as an "extremely anharmonic" interaction. The *mean* positions of the atoms form a perfect crystal; however, those positions do *not* represent any minimum of the potential energy, and the atoms will strongly fluctuate around their mean position at any temperature. Unlike a regular solid, the tethered solid may exist in a true equilibrium at both zero and negative pressures, since the infinite strength of the attractive part V_a guarantees that it will not evaporate.

Since the potential energy of the solid vanishes in any permitted configuration, its Helmholtz free energy F consists only of the trivial kinetic part ($\frac{1}{2}k_BT$ per degree of freedom) and the configurational contribution $F_c\equiv-T\mathcal{S}$, where the entropy $\mathcal{S}$ contains all the physics of the system. Note that the temperature T enters into F only as a multiplicative factor. Thus the elastic constants will be strictly proportional to T, and the system will have long-wavelength phonons whose frequency will depend on the temperature.

III. ONE-DIMENSIONAL CASE

Not surprisingly, the one-dimensional case can be treated analytically. In $d=1$ we consider a chain consisting of $N+1$ atoms (N bonds between the atoms), positioned at $x_0,x_1,\ldots,x_N$. The attractive potential V_a now acts between the pairs of the type $(i,i+1)$. While the interparticle potentials remain invariant under reflection $[V(x)=V(|x|)]$, one can easily see how this symmetry breaks in the tethered solid. For simplicity we consider the case with $b<2a$, i.e., when the maximal separation between the neighboring atoms is small enough not to permit placing of an additional atom between them: A particular order between a pair of atoms, say, $x_i<x_{i+1}$ (or $x_i>x_{i+1}$), for some i, imposes a global order $x_0<x_1<\cdots<x_{N-1}<x_N$ (or $x_0>x_1>\cdots>x_{N-1}>x_N$). Thus, right from the beginning, we could use potentials which are *not* invariant under reflection and favor a particular order of atoms. For $b>2a$, the relative position of a single pair of atoms no longer determines the orientation of the entire solid; however, for a sufficiently large chain we will again have a similar "symmetry breaking."

Thermodynamic properties of a tethered solid can be easily found in a stress ensemble: If forces f ($f>0$ for stretching) are applied to th ends of the solid and the ordering $x_i<x_{i+1}$ of the atoms is assumed, then one can easily find the partition function

$$Z_f=\frac{1}{h^2}\int e^{-H/k_BT}\prod_{i=0}^{N}dp_i\prod_{i=0}^{N-1}dy_i\ ,$$

where the integrations are performed over all particle momenta p_i and all interparticle distances $y_i\equiv x_{i+1}-x_i$, while

$$H\equiv\sum_{i=0}^{N}\frac{p_i^2}{2m}+\sum_{i=0}^{N-1}[V_a(y_i)+V_r(y_i)]-f\sum_{i=0}^{N-1}y_i\ . \tag{3.1}$$

(The second sum in this expression is just the total length of the solid.) The presence of V_a and V_r restricts the space integrals to the range $a\le y_i\le b$, and the resulting partition function is

$$Z_f=\Lambda^{-(N+1)}\left[\frac{e^{\beta fb/k_BT}-e^{\beta fa/k_BT}}{\beta f}\right]^N, \tag{3.2}$$

where $\Lambda=(\beta h^2/2\pi m)^{1/2}$, and $\beta\equiv1/k_BT$. Thus the Gibbs free energy per bond is

$$\frac{G}{N}=\frac{N+1}{N}k_BT\ln\Lambda-k_BT\ln\left[\frac{e^{\beta fb/k_BT}-e^{\beta fa/k_BT}}{\beta f}\right], \tag{3.3}$$

while the total mean size L of the solid and the mean bond length l are given by

$$l=\frac{L}{N}=\frac{\partial}{\partial f}\left[\frac{G}{N}\right]=\frac{be^{\beta fb}-ae^{\beta fa}}{e^{\beta fb}-e^{\beta fa}}-\frac{1}{\beta f}\ . \tag{3.4}$$

Not surprisingly for a very strong stretching ($f\to+\infty$), $l\to b$, while for a very strong compression ($f\to-\infty$), $l\to a$. For small forces ($f\ll1/\beta b$), one obtains

$$l=\tfrac{1}{2}(b+a)+\tfrac{1}{12}\beta(b-a)^2f\ , \tag{3.5}$$

i.e., the system has a natural size $L_0=Nl_0=\frac{1}{2}(a+b)N$, and a *harmonic* response to an external force, with force constant $k_f=12k_BT/[N(b-a)^2]$, or "elastic modulus" $C\equiv k_fL_0=[6(b+a)/(b-a)^2]k_BT$. As in polymer physics, the entropy-generated force constant is strictly proportional to the temperature. The case of a regular ("nontethered") one-dimensional fluid can be recovered in (3.2) and (3.3) by taking the $b\to\infty$ limit for $f<0$. Obviously, the expressions for Z_f and G for tethered and nontethered cases coincide for a very large compression (large negative f).

It is interesting to compare these results with approximate solutions of the same problem. In particular, we would like to know whether the approximate approaches are able to reproduce both the mean interatomic distance and the elastic constant. One might consider two simple methods.

Harmonization of the potential: This method consists of replacement of the actual square-well interparticle potential, by a harmonic spring with energy $\frac{1}{2}k_h(y_j-l_0)^2$, where the zero-force distance l_0 and the harmonic force constant k_h are chosen in such a way that they reproduce correctly the mean interatomic distance and the mean-squared fluctuations of a simple pair of atoms connected by the original potential. In such a "diatomic molecule" the thermal averages are $\langle y_j \rangle = \frac{1}{2}(a+b)$ and $\Delta \equiv \langle (y_j - \langle y_j \rangle)^2 \rangle = (b-a)^2/12$. The harmonization procedure requires one to choose $l_0 = \frac{1}{2}(a+b)$. Since Δ of a square-well potential does not depend on T, while for a harmonic oscillator it is $k_B T/k_h$, we must choose a temperature-dependent force constant

$$k_h = 12 k_B T/(b-a)^2 \ . \tag{3.6}$$

Notice that this simple procedure reproduced the exact answers, which have been obtained above.

The *mean-field* (or molecular field) approach consists of "freezing" of all atoms in the chain, except one, in their mean positions with lattice spacing l (yet to be determined), and measuring the configuration space available for the single nonfrozen atom. The "volume" of the configuration space coincides, in this case, with the length A of the segment in which the nonfrozen atom can be placed,

$$A = \begin{cases} 2(l-a) \text{ for } a < l < \dfrac{a+b}{2}, \\ 2(b-l) \text{ for } \dfrac{a+b}{2} < l < b. \end{cases} \tag{3.7}$$

Thus the mean-field estimate of the configurational part of the free energy (per atom),

$$F_c(l) = -k_B T A(l) \ , \tag{3.8}$$

is symmetric around $l = l_0 = \frac{1}{2}(a+b)$ and has a minimum at that point. (F_c does not include the l-independent kinetic energy of the atom.) Unfortunately, $\partial F(l)/\partial l$ is discontinuous at that point and one cannot obtain an estimate of the elastic constant by simple calculation of $\partial^2 F/\partial l^2$. One might obtain an estimate of the force constant by further "harmonizing" the mean-field expression for F_c, similar to the harmonization of the interparticle potential. This procedure leads to an effective force constant $k_e = 24 k_B T/(b-a)^2$, which is twice as large as the correct value of the force constant. Thus such a crude approximation produced a rather reasonable value of the force constant.

IV. TWO-DIMENSIONAL CASE

A two-dimensional tethered solid is of larger practical interest, due to its relation to tethered surfaces.[6,7] However, its free energy cannot be evaluated analytically. Thus one can only compare the predictions of approximate theories with the results of Monte Carlo simulations. I consider a case of a triangular tethered network. Figure 1 depicts an equilibrium configuration of a parallelogram excised from such a solid at zero pressure. From the point of view of elasticity, the sixfold symmetry of the triangular array is equivalent to isotropic, and can be described by the elastic stiffness tensor $C_{ijkl} = (\kappa - \mu)\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$, where κ and μ are the two-dimensional bulk and shear moduli, respectively. As in the one-dimensional case, the Helmholtz free energy of the system is proportional to T, and application of a strain will modify the free energy, only because the entropy of the system changes under the strain. The shape fluctuations of the solid will not depend on the temperature, while κ and μ will be proportional to T. Estimates of the elastic moduli can be found from (1.1). Using the Monte Carlo technique,[7] one obtains $\kappa \approx 6.8 k_B T$, $\mu \approx 5.4 k_B T$, and lattice constant $l_0 \approx 1.34$, for parameters $a = 1$ and $b = \sqrt{3}$. We will now compare those numerical estimates with the predictions of approximate theories.

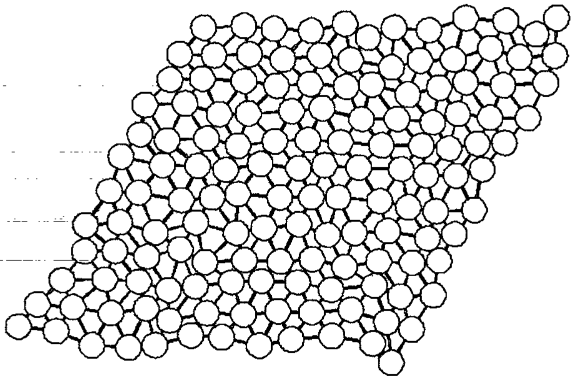

FIG. 1. Equilibrium configuration of a parallelogram excised from a two-dimensional tethered solid with a connectivity of a triangular array.

Harmonization of the square-well potential replaces the system by a regular triangular array of springs with force constants k_h. Such construction has only one independent parameter, and therefore forces a definite relation between the moduli $\kappa = 2\mu = \sqrt{3}/2 k_h$. Clearly, one cannot expect such a relation to hold in a real solid for an arbitrary choice of a and b. If one uses the one-dimensional expression (3.6) to select the value of k_h, one finds $\kappa \approx 20 k_B T$, $\mu \approx 10 k_B T$, and $l_0 \approx 1.37$. The elastic moduli are about twice as large as their Monte Carlo estimates. However, there is no obvious rule for calculation of k_h; similar results are obtained if one considers a "diatomic molecule" moving in *two* dimensions.

The mean-field approach requires freezing of all atoms, except one, in their average position, determined by the shape and size of a unit cell. Let the unit cell (parallelogram) be built of two vectors, connecting the nearest-neighbor atoms, of lengths l_1 and l_2 and forming angle α. In the equilibrium, at zero external stress we expect $l_1 = l_2$ and $\alpha = \pi/3$. The mean-field estimate of the free energy is again given by (3.8); however, in the two-dimensional case, A is the *area* in which the nonfrozen atom can be located. Both A and F_c depend on three variables l_1, l_2, and α. Area A can be found analytically, although it leads to rather complicated expressions. Figure 2(a) depicts the l dependence of $F_c(l)$ for the case $l_1 = l_2 = l$ and $\alpha = \pi/3$. Such deformation corresponds to isotropic compression and is supposed to measure κ. $F_c(l)$ is continuous, but has discontinuous derivatives, as can be clearly seen in the graph of its second derivative in Fig. 2(b). One may again attempt to determine κ by replacing the actual $F_c(l)$ by a parabolic equivalent. From

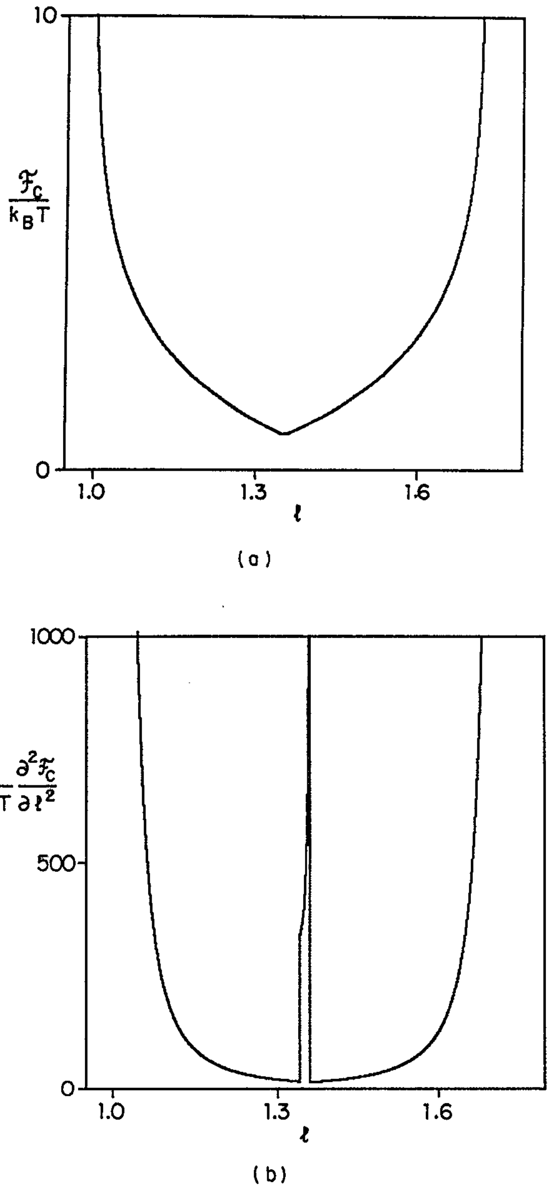

FIG. 2. Mean-field estimate of the free energy F_c (a) and its second derivative (b) as a function of the interatomic spacing l, for $a=1$, and $b=\sqrt{3}$ (see text). $F_c(l)$ has two nonanalytic points close to its minimum value.

F_c depicted in Fig. 2(a), we find the mean value of $l=l_0=1.36$, and its variance $\Delta=0.013$, which can be reexpressed in terms of harmonic force constants leading to the bulk modulus $\kappa\approx 22k_BT$. Similarly, the shear modulus μ can be calculated by considering a pure shear of the system, i.e., change of the angle α, while keeping $l_1=l_0$ and $l_2=(\sqrt{3}/2)l_0/\sin\alpha$. This procedure produces $\mu\approx 23k_BT$. We see that the mean-field approach produces a good estimate of the interparticle spacing, but significantly overestimates the elastic stiffness of the system.

The nonanalytic behavior of the mean-field estimate of F_c is a direct consequence of the abrupt changes in the chosen potential. It could be removed by the use of "softer" rapidly varying analytic potentials. However, such a change would not significantly improve the accuracy of the mean-field solution, unless the assumed potentials are almost harmonic, since the above results demonstrate the lack of relation between the curvature of the mean-field approximation of F_c at its minimum and the elastic constants of the solid.

V. DISCUSSION

The tethered solid model, whose behavior is solely determined by entropic considerations, complements the usual approach to the solid, and provides some insight into the behavior of a system with strongly anharmonic potentials, as well as serves as a toy example of entropy-generated elasticity. Simple harmonization and mean-field approaches have been shown to produce a good estimate of the interparticle spacing, and order-of-magnitude estimates of the elastic moduli. The mean-field approach can be systematically improved by considering several nonfrozen atoms.

The model is related to the rigid-sphere models, and in the limit of large external pressures will have similar physical properties. However, unlike the rigid-sphere models, it does not have a liquid phase, and, consequently, cannot be used to investigate melting. On the other hand, depending on the choice of a particular tethering of the atoms, there may be several solid phases and one may address more interesting questions, such as structural phase transitions (under external pressure) of strongly fluctuating systems. The model provides a simple demonstration of the emergence of harmonic response from a nonharmonic potential. It can also be used to investigate some aspects of topological entanglements in macromolecules.

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[1] See, e.g., J. H. Weiner, *Statistical Mechanics of Elasticity* (Wiley, New York, 1983).

[2] See, e.g., C. F. Squire, Phys. Rev. **151**, 689 (1966); O. G. Paterson, D. N. Batchelder, and R. O. Simmons, Philos. Mag. **12**, 1193 (1965).

[3] F. H. Stillinger, Phys. Rev. **142**, 237 (1966); F. H. Stillinger and Z. W. Salsburg, J. Chem. Phys. **46**, 3962 (1967); K. Honda, H. Nakano, and K. Nakomura, J. Phys. Soc. Jpn. **49**, 456 (1980).

[4] M. Parinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980); J. Chem. Phys. **80**, 4423 (1983).

[5] For review, see D. J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1979); P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[6] Y. Kantor, M. Kardar, and D. R. Nelson, Phys. Rev. Lett. **57**, 791 (1986); Phys. Rev. A **35**, 3056 (1987); M. Kardar and D. R. Nelson, Phys. Rev. Lett. **58**, 1298 (1987).

[7] Y. Kantor and D. R. Nelson, Phys. Rev. Lett. **58**, 2774 (1987); Phys. Rev. A **36**, 4020 (1987).

[8] S. Leibler, R. R. P. Singh, and M. E. Fisher, Phys. Rev. Lett. **59**, 1989 (1987).

[9] I. Carmesin and K. Kremer (unpublished).