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Elasticity of Gaussian and nearly Gaussian phantom networks

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We study the elastic properties of phantom networks of Gaussian and nearly Gaussian springs. We show that the stress tensor of a Gaussian network coincides with the conductivity tensor of an equivalent resistor network, while its elastic constants vanish. We use a perturbation theory to analyze the elastic behavior of networks of slightly non-Gaussian springs. We show that the elastic constants of phantom percolation networks of nearly Gaussian springs have a power-law dependence on the distance of the system from the percolation threshold, and we derive bounds on the exponents.

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I. INTRODUCTION

Rubber and gels are large polymeric solid networks formed when polymers or monomers in fluid solutions are randomly cross-linked by permanent bonds. This process is called vulcanization or gelation, where the latter term usually applies to cross-linking of monomers or very short polymers—gels, while the former term usually describes the formation of dense networks of long polymers — rubber. Rubber and gels are much more flexible than ordinary crystalline solids and, moreover, may remain in the linear elastic regime even in response to deformations increasing their dimensions far beyond their original, unstrained, size. Such a behavior is attributed to the network structure of these materials, and to the fact that the elastic restoring forces are of entropic, rather than energetic, origin. The simplest theory of *rubber elasticity* which captures these essential physical features is the ''phantom network'' (PN) model introduced by James and Guth [1]. This model assumes that the configurations of the different polymer chains are independent of each other, and neglects the excluded volume interactions between the monomers. With these simplifying assumptions one can treat each polymer chain in the network as an ideal one. By averaging over the positions of the monomers one finds that the probability density of finding chain ends separated by $\vec{r}$ takes a Gaussian form $\sim\exp[-\frac{1}{2}Br^2]$, where B usually depends on the temperature T. The free energy of the chain is proportional to (minus) the logarithm of this probability density and, therefore, is proportional to r^2, as if it is a linear spring of vanishing equilibrium length, which will be called *Gaussian spring*. In the PN model, the thermal averages of some quantities can be calculated analytically due to the Gaussian form of the statistical weights [2], and this makes it an excellent starting point for models with excluded volume interactions and entanglements [3].

The problem of *gel elasticity* introduces an additional complication already at the level of the PN model. In gels the network strands are very short and do not necessarily resemble Gaussian springs. Nevertheless, one may still construct a Gaussian model of gel elasticity simply by replacing each bond of the gel by a Gaussian spring. In the absence of excluded volume interactions, the validity of this model is justified by the fact that even if the elementary pair potential between bonded atoms is very different from that of a Gaussian spring, the *effective* interaction between somewhat more distant atoms is, almost always, quadratic. This is a well-known feature of long polymer chains [4], but it has also been demonstrated for more complicated networks [5]. de Gennes used an analogy between the elasticity of networks of Gaussian springs and the conductivity of random resistor networks [6], and argued that rigidity, just like conductivity, appears at the connectivity threshold, when a macroscopically large network spans the system. He further argued that at the phase transition the shear modulus and the conductivity should have the same dependence on the distance of the system from the connectivity threshold. Surprisingly, the details of the argument of de Gennes have never been worked out, i.e., there is no detailed calculation of the quantities characterizing the elastic response of Gaussian networks, namely the stress and elastic constants tensors. [There are several analytical studies of the statistical properties (including the elastic properties) of systems of Gaussian springs [2,7], but none of them makes such an explicit calculation.] In Sec. II of this paper we derive exact results for the stress and elastic constants of Gaussian networks. We prove that the stress *tensor* of a Gaussian elastic network is *equal* to the conductivity *tensor* of an equivalent resistor network. A detailed proof of this equality, which holds for a Gaussian network of arbitrary topology, is given in the Appendix of the paper. We also show that the elastic constants of a system consisting of a single spanning cluster of Gaussian springs *vanish*. We discuss the effect of the finite clusters which model the small molecules formed in the process of cross-linking and show that they play a crucial role in stabilizing the system.

In Sec. III we investigate the elastic behavior of phantom networks of nearly Gaussian springs, whose energy dependence on their extension includes a small quartic term additional to the quadratic one. A perturbative analysis yields an expression for the elastic constants. In Sec. IV we use this expression to evaluate the elastic constants of phantom percolation networks [8], close to the percolation threshold p_c. We conjecture a universal scaling law for the elastic constants, $C\sim(p-p_c)^g$, and derive exact bounds for the scaling exponent g. Section V includes a short summary and discussion of the main results.

II. ELASTICITY OF SYSTEMS OF GAUSSIAN SPRINGS—EXACT RESULTS

A. Definitions in the theory of elasticity

The theory of elasticity describes deformations of thermodynamic systems in response to external forces. At a finite temperature, it is convenient to consider *homogeneous* deformations of the *boundaries* of the system, which can be described by a *constant* matrix M_{ij}. When the system is strained, the separation between a pair of surface points, which prior to the deformation was $\vec{R}$, changes to

$$r_i = M_{ij} R_j, \tag{1}$$

where the subscripts denote Cartesian coordinates, and summation over repeated indices is implied. Usually the energy of the system depends on the relative distances between the atoms. The squared distance in the deformed system is equal to

$$r^2 = r_k r_k = M_{ki} R_i M_{kj} R_j = (M^t M)_{ij} R_i R_j \equiv (\delta_{ij} + 2\eta_{ij}) R_i R_j, \tag{2}$$

where M^t is the transpose of M, and η_{ij} is the *strain* tensor, while δ_{ij} is the Krönecker delta. The strain tensor vanishes at the undeformed reference state. Expanding the mean free energy density in the strain variables

$$f(\{\eta\}) = f(\{0\}) + \sigma_{ij}\eta_{ij} + \frac{1}{2} C_{ijkl}\eta_{ij}\eta_{kl} + \cdots, \tag{3}$$

we identify the coefficients σ_{ij} as the components of the *stress* tensor, while C_{ijkl} are the *elastic constants* (sometimes referred to as the *elastic stiffness tensor*). The elastic constants of a thermodynamic system are related to each other through certain equalities. The actual number of independent elastic constants depends on the symmetries of the system. Isotropic systems, for instance, have only three *different* nonvanishing elastic constants: $C_{11} \equiv C_{xxxx} = C_{yyyy} = C_{zzzz}$; $C_{12} \equiv C_{xxyy} = C_{yyzz} = C_{zzxx} = \cdots$; and $C_{44} \equiv \frac{1}{2}(C_{xyxy} + C_{xyyx}) = \cdots$. Moreover, these three elastic constants obey an additional relation [9]: $C_{11} - C_{12} = 2C_{44}$, which reduces the number of independent elastic constants of isotropic systems to two. Frequently, one finds it more useful to describe the elastic behavior in such systems in terms of the *shear* modulus μ and the *bulk* modulus κ, defined by [10]

$$\mu = C_{44} - P, \tag{4}$$

and

$$\kappa = \begin{cases} \frac{1}{2}(C_{11} + C_{12}) & \text{for two-dimensional systems} \\ \frac{1}{3}(C_{11} + 2C_{12} + P) & \text{for three-dimensional systems,} \end{cases} \tag{5}$$

where $P = -\sigma_{xx} = -\sigma_{yy} = -\sigma_{zz}$ is the pressure. When κ and μ are positive, the system is mechanically stable [11].

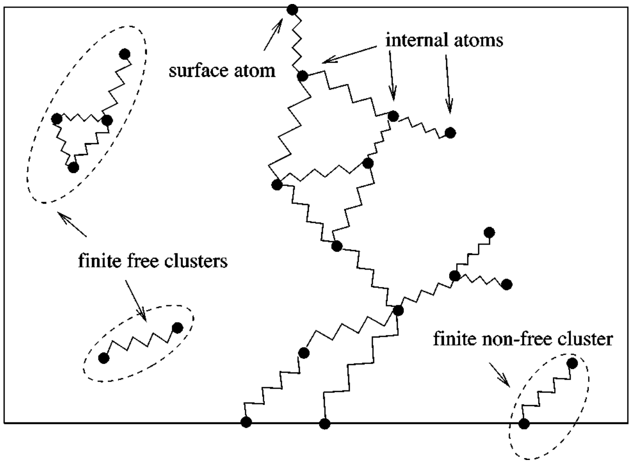

FIG. 1. A schematic picture of a network of springs. The system includes a spanning elastic network as well as some finite clusters. Atoms can be either internal, i.e., free to move inside the volume, or external, i.e., attached to a permanent positions on the boundaries. Non-free-clusters have at least one external atom.

B. Description of the system

We consider a d-dimensional system shown schematically in Fig. 1. The black circles in Fig. 1 represent atoms while the zigzag lines indicate the bonds, attractive pair-potentials, which connect them in a certain fixed (quenched) topology. Atoms that are found inside the volume of the systems are called *internal* atoms. *Surface* atoms have fixed coordinates on the boundaries of the system. The bonds connect atoms into clusters. Clusters containing only internal atoms are *free* to move in the entire volume. Clusters with both internal and surface atoms are non-free. Among them, one (and, in some cases, several) may extend from one side of the system to the opposite side. This is the ‘‘spanning’’ cluster.

The system that we study in this section consists of point-like atoms connected by Gaussian springs. The energy of each Gaussian spring is given by

$$\phi_{\alpha\beta}(\vec{R}^{\alpha} - \vec{R}^{\beta}) = \frac{1}{2} K^{\alpha\beta} (\vec{R}^{\alpha} - \vec{R}^{\beta})^2 = \frac{1}{2} K^{\alpha\beta} (R^{\alpha\beta})^2, \tag{6}$$

where $\vec{R}^{\alpha}$ and $\vec{R}^{\beta}$ denote the positions of atoms α and β, and $R^{\alpha\beta}$ is the distance between these atoms. The spring constant $K^{\alpha\beta}$ is assumed to have a fixed, *temperature-independent*, value. The total elastic energy is given by the sum over the energies of all the springs

$$E = \sum_{\langle\alpha\beta\rangle} \phi_{\alpha\beta} = \sum_{\langle\alpha\beta\rangle} \frac{1}{2} K^{\alpha\beta} (R^{\alpha\beta})^2.$$

C. Elasticity of the system

The components of the stress tensor of our system are related to the pair potentials, $\phi_{\alpha\beta}(R^{\alpha\beta})$, via the relation

$$\sigma_{ij} = \frac{1}{V} \left\langle \sum_{\langle\alpha\beta\rangle} \phi'_{\alpha\beta}(R^{\alpha\beta}) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \right\rangle - \frac{NkT\delta_{ij}}{V}, \tag{7}$$

which was derived 30 years ago by Squire, Holt, and Hoover [12] as an extension of the Born and Huang theory of elasticity [13] to systems at finite temperature. In expression (7) summation over all distinct pairs of atoms, $\alpha\beta$, is performed, where $R_i^{\alpha\beta}$ and $R_j^{\alpha\beta}$ are the ith and the jth Cartesian components of $\vec{R}^{\alpha\beta}\equiv\vec{R}^{\alpha}-\vec{R}^{\beta}$. The symbol $\langle\ \rangle$ indicates a thermal average, while N and V denote the number of internal atoms and the volume of the system, respectively. For potential (6) the expression (7) reduces to

$$\sigma_{ij}=\frac{1}{V}\left\langle \sum_{\langle\alpha\beta\rangle} K^{\alpha\beta}R_i^{\alpha\beta}R_j^{\alpha\beta}\right\rangle-\frac{NkT}{V}\delta_{ij}, \tag{8}$$

where the sum is over the connected pairs.

The two terms in expression (8) are called the configurational and kinetic terms, respectively. The configurational term can be divided into terms, each one including the sum over the bonds of one distinct cluster. Since there are no excluded volume interactions, these terms are independent of each other (the clusters do not interact with each other), and the contributions of the different clusters to the stress are additive. We identify the stress applied by each cluster as

$$\sigma_{ij}^{\text{cluster}}=\frac{1}{V}\left\langle \sum_{\langle\alpha\beta\rangle\in\text{cluster}} K^{\alpha\beta}R_i^{\alpha\beta}R_j^{\alpha\beta}\right\rangle-\frac{N_IkT}{V}\delta_{ij}, \tag{9}$$

where N_I is the number of internal atoms of the cluster.

D. The contribution of the free clusters

The gas of free clusters is an ideal gas. Since the different clusters do not ''feel'' each other, it is intuitively clear that the contribution to the stress of each free cluster (fc) should be as of a pointlike atom. To prove this result (which is general and does not depend on the particular form of the pair potential), we use the fact that for a free cluster, one can integrate out d degrees of freedom (of say, $\vec{R}^1$) in Eq. (9), and express the terms appearing in it in the relative coordinates $\tilde{R}_i^{\alpha}=R_i^{\alpha}-R_i^1$ $\{\alpha=2,\ldots,N_I\}$. (This statement is correct only in the thermodynamic limit, when the linear size of the system becomes much larger than the radius of gyration of the free cluster.) One can easily verify that in the relative coordinates Eq. (9) may also be written in the following way:

$$\sigma_{ij}=\frac{1}{V}\left\langle \sum_{\alpha=2}^{N_I}\tilde{R}_i^{\alpha}\frac{\partial E}{\partial\tilde{R}_j^{\alpha}}\right\rangle-\frac{N_IkT}{V}\delta_{ij},$$

which from the equipartition theorem gives $\sigma_{ij}=-(kT/V)\delta_{ij}$. The stress applied by *all* the free clusters is simply

$$\sigma_{ij}^{\text{fc}}=-\frac{N_0kT}{V}\delta_{ij}, \tag{10}$$

where N_0 is the total number of free clusters. Similarly, the contribution of the free clusters to the elastic constants is also as of an ideal gas, given by the kinetic term [12]

$$C_{ijkl}^{\text{fc}}=\frac{2N_0kT}{V}\delta_{il}\delta_{jk}. \tag{11}$$

E. Elasticity of the spanning cluster

The stress and elastic constants of the spanning network of Gaussian springs with temperature-independent force constants are temperature independent. The free energy F of the spanning network is a function of the temperature T and the positions of the surface atoms $\{\vec{R}^s\}$. If the values of these variables change quasi statically, then

$$dF=-SdT+\sum_s \vec{f}_{\text{ext}}^{s}\cdot d\vec{R}^s, \tag{12}$$

where S is the entropy, $\vec{f}_{\text{ext}}^{s}$ is the external force which drags the surface atom s, and summation is made over all the surface atoms. In a quasistatic process, the force $\vec{f}_{\text{ext}}^{s}$ is balanced by the force $\vec{f}^s$ applied by the network on atom s, namely,

$$-\vec{f}_{\text{ext}}^{s}=\vec{f}^s=\left\langle \sum_{\alpha} K^{\alpha s}(\vec{R}^{\alpha}-\vec{R}^s)\right\rangle, \tag{13}$$

where summation is over all atoms α connected to atom s. The terms appearing in the thermal average in Eq. (13) are linear in the coordinates $\vec{R}^{\alpha}$. Since the Boltzmann weight is a Gaussian, i.e., an exponent of a quadratic form of the coordinates, these averages coincide with the most probable values, namely their values at the energetic ground state, and therefore do not depend on the temperature. We thus conclude that $\vec{f}^s$ is a temperature-independent quantity, and from Eqs. (12) and (13) we readily find that

$$\frac{\partial^2 F}{\partial T\partial\vec{R}^s}=-\frac{\partial\vec{f}^s}{\partial T}=0.$$

The last result implies that F can be decomposed into two parts

$$F(T,\{\vec{R}^s\})=F_1(T)+F_2(\{\vec{R}^s\}).$$

If we consider homogeneous deformations we may define a reference system and use the strain variables $\{\eta_{ij}\}$, instead of $\{\vec{R}^s\}$,

$$F=F_1(T)+F_2(\{\eta_{ij}\}).$$

The stress and elastic constants are the coefficients in the $\{\eta\}$ expansion of F_2 [see Eq. (3)]. Therefore, they do not depend on the temperature.

The stress applied by the spanning network is equal to the conductivity of a resistor network with the same topology. The stress of the spanning cluster (spc) [Eq. (9)]

$$\sigma_{ij}^{\text{spc}}=\frac{1}{V}\left\langle \sum_{\langle\alpha\beta\rangle\in\text{spc}} K^{\alpha\beta}R_i^{\alpha\beta}R_j^{\alpha\beta}\right\rangle-\frac{N_IkT}{V}\delta_{ij},$$

can be rewritten in the form

$$\sigma_{ij}^{\mathrm{spc}}=\frac{1}{V}\left\{\left\langle\sum_{\alpha=1}^{N_I}R_i^{\alpha}\frac{\partial E}{\partial R_j^{\alpha}}\right\rangle+\left\langle\sum_{\langle\alpha s\rangle\in\mathrm{spc}}K^{\alpha s}R_i^{s}R_j^{s\alpha}\right\rangle\right\}-\frac{N_I kT}{V}\delta_{ij}, \tag{14}$$

where the first sum is over all the internal atoms while the second sum is over all the bonds connecting internal and surface atoms. (The subscripts s and α denote surface and internal atoms, respectively.) In the thermodynamic limit we deduce from the equipartition theorem that the first and the third (kinetic) terms in Eq. (14) cancel each other. We are thus left only with the second term

$$\sigma_{ij}^{\mathrm{spc}}=\frac{1}{V}\left[\sum_{\langle\alpha s\rangle\in\mathrm{spc}}K^{\alpha s}R_i^{s}\langle R_j^{s\alpha}\rangle\right]. \tag{15}$$

The thermal averages in Eq. (15) are of quantities which are linear in the coordinates of the internal atoms and therefore may be replaced by the equilibrium values of these quantities (see earlier in this section). The equilibrium values of $\vec{R}^{\alpha}$ minimize the energy of the spanning cluster

$$\begin{aligned}E^{\mathrm{spc}}&=\sum_{\langle\alpha\beta\rangle\in\ \mathrm{spc}}\frac{1}{2}K^{\alpha\beta}(\vec{R}^{\alpha}-\vec{R}^{\beta})^2\\&=\sum_{j=1}^{d}\left[\sum_{\langle\alpha\beta\rangle\in\mathrm{spc}}\frac{1}{2}K^{\alpha\beta}(R_j^{\alpha}-R_j^{\beta})^2\right]\\&\equiv\sum_{j=1}^{d}E_j^{\mathrm{spc}}.\end{aligned} \tag{16}$$

The dependence of E^{spc} on the components R_j^{α} corresponding to one Cartesian direction j is included in the term E_j^{spc}. The problem of finding the equilibrium values of $\vec{R}^{\alpha}$ decouples into d scalar problems of finding the equilibrium values of R_j^{α}. In order to calculate these values we need to solve d sets of the linear equation (one set for each Cartesian component),

$$\sum_{\beta}K^{\alpha\beta}(R_j^{\alpha}-R_j^{\beta})=0, \tag{17}$$

corresponding to the vanishing of the jth component of the force acting on each internal atom. (For each atom α, summation in the relevant equation is over all atoms β connected to it.)

Let us define a resistor network with the same connectivity as the elastic network, in which each spring is replaced by a resistor with conductance $K^{\alpha\beta}$. The values of the electric potential at the internal nodes, $\{\varphi^{\alpha}\}$, are obtained by minimization of the heat power produced in the network, $P=\Sigma_{\langle\alpha\beta\rangle}K^{\alpha\beta}(\varphi^{\alpha}-\varphi^{\beta})^2$. Except for a prefactor of $\frac{1}{2}$, P is identical with E_j^{spc} (16), where φ^{α} plays the role of R_j^{α}. If we replace R_j^{α} by φ^{α} in the force equations (17), we obtain the set of Kirchoff equations enforcing the vanishing of the sum of currents entering the internal nodes of the network. By replacing R_j^{α} by φ^{α}, we define a mapping of the mechanical problem to an electrostatic one. In fact, we have d different electrostatic problems corresponding to each Cartesian component of the mechanical problem. They differ from each other in their boundary conditions, namely the values of the electric potential on the surface nodes, $\{\varphi^{s}\}$. In the jth electrostatic problem, we set φ^{s} equal to R_j^{s}, i.e., we assume that the electric potential at each boundary point is equal to the jth Cartesian coordinate of the point.

The interesting question now is what is the analog of the stress tensor in the electrostatic problem. This appears to be the conductivity tensor Σ_{ij} defined by

$$\langle j_i\rangle=\Sigma_{ij}\langle E_j\rangle,$$

where $\langle\vec{j}\rangle$ and $\langle\vec{E}\rangle$ are the *volume averages* of the current density and the electric field, respectively. More precisely, if we follow the mapping defined above we have the *exact* equality

$$\sigma_{ij}=\Sigma_{ij}. \tag{18}$$

A detailed proof of this equality is given in the Appendix to this paper. Here we just note that the proof consists of two steps: In the first step we show that in the jth electrostatic problem, because of the choice of boundary conditions, $\langle\vec{E}\rangle$ is a unity electric field pointing in the $(-j)$th direction. In the presence of such an electric field $\langle j_i\rangle=-\Sigma_{ij}$. On the next step of the proof we show that $-\langle j_i\rangle$, and therefore Σ_{ij} are given by the electrostatic equivalent of Eq. (15)

$$\Sigma_{ij}^{\mathrm{spc}}=\frac{1}{V}\left[\sum_{\langle\alpha s\rangle\in\mathrm{spc}}K^{\alpha s}R_i^{s}(\varphi^{s}-\varphi^{\alpha})\right], \tag{19}$$

and therefore Eq. (18) is valid.

The elastic constants of the spanning network vanish. We have already shown that C_{ijkl}, the elastic constants of the spanning cluster of Gaussian springs with temperature-independent force constants, are temperature independent. Therefore, we may calculate them at any temperature, and in particular at $T=0$. At zero temperature the free energy coincides with the internal energy, given by Eq. (16), where $\{\vec{R}^{\alpha}\}$, the positions of the internal nodes, take their equilibrium values. Suppose now that the system is homogeneously strained. The positions of the surface nodes, $\{\vec{R}^{s}\}$, change according to the linear transformation (1), with a constant matrix M_{ij}. [Transformation (1) was originally defined for the separation between surface points. However, we can always set the origin of axes to be on the original (unstrained) surface, and in this case the transformation applies to the positions of the surface points.] In order to find the new equilibrium positions of the internal atoms in the strained system, we need to solve the set of equations (17) with the new boundary conditions. Since both the equations and the transformation of the boundary conditions are linear, the new solution is given by $r_i^{\alpha}=M_{ij}R_j^{\alpha}$. The elastic energy of the strained spanning cluster is given by [see Eqs. (2) and (16)]

$$\begin{aligned}E^{\mathrm{spc}}&=\frac{1}{2}\sum_{\langle\alpha\beta\rangle\in\ \mathrm{spc}}K^{\alpha\beta}(r^{\alpha\beta})^2\\&=\frac{1}{2}\sum_{\langle\alpha\beta\rangle\in\ \mathrm{spc}}K^{\alpha\beta}[(M^tM)_{ij}R_i^{\alpha\beta}R_j^{\alpha\beta}]\\&=\frac{1}{2}\sum_{\langle\alpha\beta\rangle\in\ \mathrm{spc}}K^{\alpha\beta}[(2\eta_{ij}+\delta_{ij})R_i^{\alpha\beta}R_j^{\alpha\beta}].\end{aligned}$$

This gives the dependence of E on the strain variables, which include only linear terms in η_{ij}. Since the elastic constants are the coefficients of the quadratic terms in the $\{\eta\}$ expansion of the free energy [Eq. (3)], we conclude that

$$C_{ijkl}^{\mathrm{spc}}\equiv 0. \qquad (20)$$

F. The stability of systems of Gaussian springs

We have mentioned earlier in this section that stable solid thermodynamic systems have positive bulk and shear moduli, κ and μ [Eqs. (4) and (5)]. In phantom systems, the contributions of the spanning cluster and the ensemble of free clusters to κ and μ are additive. Due to the vanishing of the elastic constants of the spanning cluster (20), we find that its contribution to the elastic moduli is $\mu^{\mathrm{spc}}=-P^{\mathrm{spc}}>0$, and $\kappa^{\mathrm{spc}}=0$ (two dimensions) or $\kappa^{\mathrm{spc}}=P^{\mathrm{spc}}/3<0$ (three dimensions) [P^{spc} is the negative (stretching) pressure applied by the spanning cluster]. The fact that κ is not positive means that the spanning cluster alone is not stable against homogeneous volume fluctuations. The contribution of the free clusters to the elastic moduli is as of an ideal gas, given by $\mu^{\mathrm{fc}}=0$ and $\kappa^{\mathrm{fc}}=N_0kT/V$ [see Eqs. (4), (5), (10), and (11)]. The vanishing of the shear modulus simply indicates that the collection of free clusters is a fluid. The positive contribution of the free clusters to the bulk modulus is crucial for the stability of the system. Two-dimensional Gaussian networks are stabilized in the presence of free clusters since $\kappa=\kappa^{\mathrm{spc}}+\kappa^{\mathrm{fc}}=\kappa^{\mathrm{fc}}>0$. Three-dimensional systems are stabilized provided that the positive contribution of the free clusters to κ overcomes the negative contribution of the spanning cluster.

In real gels, it is possible to wash out the finite clusters (or most of them) and obtain a so-called dry gel. Within the Gaussian model such a system is expected to be unstable. This contradicts experimental observations and demonstrates the importance of excluded volume (EV) and entanglements' effects. In the presence of EV interactions, the polymer chains forming the network cannot be treated as Gaussian springs. Therefore, the elastic constants of such networks do not vanish, and consequently, there is no simple relation between the pressure and the elastic moduli. Moreover, EV interactions make a positive contribution to the pressure which may, therefore, be both positive or negative. In dense systems, EV interactions may effectively cancel out [4]. However, dense systems can only be achieved in the presence of the finite clusters. In that case different clusters interact with each other, and their contributions to the pressure and elastic moduli are not additive. In the following section we consider a different correction to the Gaussian model: without EV interactions but with a non-Gaussian pair potential.

III. ELASTICITY OF SYSTEMS OF NEARLY GAUSSIAN SPRINGS

The elastic response of polymers and polymeric networks is as of systems of Gaussian springs only in the first approximation. It always includes a nonlinear part, which becomes significant when the network is sufficiently stretched, much beyond its characteristic thermal lengths [1,14]. In order to study the nature of this correction, we consider networks of springs having the spring energies

$$\phi_{\alpha\beta}(R^{\alpha\beta})=\frac{1}{2}K^{\alpha\beta}(R^{\alpha\beta})^2+\frac{1}{4}a^{\alpha\beta}(R^{\alpha\beta})^4. \qquad (21)$$

Our choice for the spring energy is inspired by the free energy of a finite long polymer chain [1], where the leading correction to the linear relation between the force and the chain end-to-end vector $\vec{f}=K\vec{R}$ is a term proportional to $R^2\vec{R}$. The elastic energy of the system is given, again, as the sum of all springs energies

$$\begin{aligned}E&=\sum_{\langle\alpha\beta\rangle}\phi_{\alpha\beta}\\&=\sum_{\langle\alpha\beta\rangle}\left[\frac{1}{2}K^{\alpha\beta}(R^{\alpha\beta})^2+\frac{1}{4}a^{\alpha\beta}(R^{\alpha\beta})^4\right]\\&\equiv E_0+E_1.\end{aligned} \qquad (22)$$

We assume that $E_1\ll E_0$, and we treat the quartic term perturbatively. In fact, we will make a more restrictive assumption that for each bond $a^{\alpha\beta}(R^{\alpha\beta})^4\ll K^{\alpha\beta}(R^{\alpha\beta})^2$. Since the quadratic term E_0 does not make any contribution to the elastic constants, we will mainly focus on the contribution of the perturbation term E_1 to them.

In the lowest order of a perturbation theory, the elastic constants of the network are temperature independent. Substituting the pair potential (22) into expression (7) for the stress tensor, and expanding this expression to the first order in $a^{\alpha\beta}$, yields

$$\begin{aligned}\sigma_{ij}=\sigma_{ij}^0&+\frac{1}{V}\left\langle\sum_{\langle\alpha\beta\rangle}a^{\alpha\beta}(R^{\alpha\beta})^2R_i^{\alpha\beta}R_j^{\alpha\beta}\right\rangle_0\\&-\frac{1}{VkT}\left\langle\delta\left(\sum_{\langle\alpha\beta\rangle}K^{\alpha\beta}R_i^{\alpha\beta}R_j^{\alpha\beta}\right)\delta E_1\right\rangle_0,\end{aligned} \qquad (23)$$

where $\delta A\equiv A-\langle A\rangle_0$ denotes a thermal fluctuation of the quantity A, and $\langle\ \rangle_0$ denotes a thermal average with the (unperturbed) Gaussian Boltzmann weight $\exp(-E_0/kT)$. σ_{ij}^0 is the stress tensor of the corresponding Gaussian network (where $a^{\alpha\beta}\equiv 0$), given by Eq. (8), which can be also expressed by its value at $T=0$

$$\sigma_{ij}^0=\frac{1}{V}\sum_{\langle\alpha\beta\rangle}[K^{\alpha\beta}(R_0^{\alpha\beta})_i(R_0^{\alpha\beta})_j]. \qquad (24)$$

In the above expression $(R_0^{\alpha\beta})_i$ is the ith Cartesian component of the bond vector $\vec{R}_0^{\alpha\beta}$ at the ground state of the unperturbed Gaussian network.

The next step is to substitute the pair potential (22) into the expression for the elastic constants [12] [see also Eq. (7) in Ref. [15]]. By expanding this expression to the first order in $\{a^{\alpha\beta}\}$, and using the fact that for the Gaussian network $C_{ijkl}\equiv 0$ (20), we find that

$$C_{ijkl}=\frac{2}{V}\left\langle \sum_{\langle\alpha\beta\rangle} a^{\alpha\beta}R_i^{\alpha\beta}R_j^{\alpha\beta}R_k^{\alpha\beta}R_l^{\alpha\beta}\right\rangle_0+\langle X\rangle_0,$$

where X is a combination of terms, each of which includes the thermal fluctuations of some quantities. Since at $T=0$ there are no thermal fluctuations, that term vanishes and we readily find that

$$\begin{aligned}C_{ijkl}(T=0)&=\frac{2}{V}\left\langle \sum_{\langle\alpha\beta\rangle} a^{\alpha\beta}R_i^{\alpha\beta}R_j^{\alpha\beta}R_k^{\alpha\beta}R_l^{\alpha\beta}\right\rangle_0\\&=\frac{2}{V}\sum_{\langle\alpha\beta\rangle}[a^{\alpha\beta}(R_0^{\alpha\beta})_i(R_0^{\alpha\beta})_j(R_0^{\alpha\beta})_k(R_0^{\alpha\beta})_l].\end{aligned}\tag{25}$$

The second equality in the above equation is obtained by equating the expression inside $\langle\ \rangle_0$ to its value at equilibrium (at zero temperature the thermal average coincides with this value).

At a finite temperature we may write the elastic constants as the product of $C_{ijkl}(T=0)$, and a dimensionless function, which may depend only on terms of the form $(kT\,a^{\alpha\beta})/(K^{\gamma\delta}K^{\epsilon\zeta})$. Expanding the function into a power series in these variables yields

$$C_{ijkl}=C_{ijkl}(T=0)\left[1+\left(\text{linear terms in}\left\{\frac{kT\,a^{\alpha\beta}}{K^{\gamma\delta}K^{\epsilon\zeta}}\right\}\right)+\cdots\right].$$

Since $C_{ijkl}(T=0)$ is a linear function in the quantities $a^{\alpha\beta}$, and since we are interested only in the first-order correction due to the perturbation (namely, in terms linear in $a^{\alpha\beta}$), we conclude that to the lowest order in $a^{\alpha\beta}$, C_{ijkl} are temperature independent, and are therefore given by the above expression (25).

IV. ELASTICITY OF PHANTOM PERCOLATION NETWORKS

A. The percolation model

One of the models which has been proposed to describe the process of gelation is *percolation* [8]. In the percolation model, the sites or the bonds of a lattice are randomly occupied by, respectively, atoms or bonds, with an occupation probability p. In the site percolation model, one links every two neighboring occupied sites, while in the bond percolation model one assumes that all the sites are occupied by atoms and each pair of neighbors is linked if the bond between the atoms exists. Within the percolation model, the gel point is identified with the percolation threshold, the critical site or bond concentration above which a spanning cluster is formed. The percolation model predicts that close to the percolation threshold, p_c, quantities such as the mean cluster mass, typical cluster linear size, and the gel fraction have power-law dependence on $(p-p_c)$. The relevant exponents are universal and depend only on the dimensionality of the system, but not on the atomic-scale features of the system. The values of these exponents have been measured experimentally for various gel systems [16]. A fairly good agreement has been found between the measured exponents and their values as predicted by the percolation model, which proves the applicability of the percolation model to gelation.

The situation concerning the elastic behavior of gels is not that clear. The main question is whether the shear modulus also follows a scaling law $\mu\sim(p-p_c)^f$ with a universal exponent *f*. Experimental values of this exponent measured for different polymeric systems are very scattered [17]. On the theoretical side, it has been demonstrated that at $T=0$, the elastic behavior of percolation systems depends on the nature of the interactions in the system. For nonstressed central force networks the rigidity threshold occurs at a concentration of bonds much larger than p_c [18]. If bond-bending forces are present, rigidity and percolation thresholds coincide; however, the rigidity exponent *f* is considerably larger than the conductivity exponent *t*, suggesting that the two problems belong to different universality classes [19]. As the number of models of elasticity of random systems increased, it became clear that de Gennes's conjecture about the identity of the exponent *f* to the conductivity exponent *t* [6] can be justified only within models which ''reduce'' the thermodynamic behavior of gels to so-called ''scalar elasticity'' models [20]. Recently, the equality $f=t$ was measured by Plischke *et al.* in a numerical study of *phantom* central force percolation networks at $T\neq 0$ [21]. The authors attributed this elastic behavior to the entropic part of the elastic free energy.

B. Elasticity of percolation networks

We would like to apply our results from Secs. II and III to phantom percolation networks of identical springs having the energy $E=\frac{1}{2}KR^2$ (Gaussian network) or $E=\frac{1}{2}KR^2+\frac{1}{4}aR^4$ (nearly Gaussian network). We discuss the critical elastic behavior of such networks in the regime where the correlation length $\xi\sim(p-p_c)^{-\nu}$ is much larger than the characteristic atomic length scale *b*, but much smaller than the linear size of the system *L*. The correlation length is the length scale below which the spanning cluster has a fractal structure and above which the system is homogeneous. A quantity that follows a power law as $(p-p_c)^Y\sim\xi^{-(Y/\nu)}$ when $L\gg\xi$ scales as $L^{-(Y/\nu)}$ when $\xi\gg L$. (At p_c the latter power law is always relevant because ξ is infinite.) Since $\xi\gg b$, we expect the structure of the spanning cluster to ''forget'' the details of the lattice, and have the elastic properties of an isotropic system. In the Gaussian case, the tensorial equality $\sigma_{ij}=\Sigma_{ij}$ (18) becomes a scalar equality $-P=\Sigma$. Also, because of the vanishing of the elastic constants of Gaussian networks (20), we have for the shear modulus of the spanning cluster that $\mu=C_{44}-P=-P=\Sigma$ (4). Close to the percolation threshold, the conductivity scales as $\Sigma\sim(p-p_c)^t$, and therefore we conclude that for Gaussian networks

$$\mu=-P=\Sigma\sim(p-p_c)^t, \tag{26}$$

in accordance with de Gennes's argument. This result is not changed if we also include the finite clusters, since the latter make no contribution to the shear modulus (just as they do not contribute to the conductivity of the system). The equality of the shear modulus and the stress, a signature of Gaussian elasticity, was observed numerically in Ref. [21].

In the nearly Gaussian case, we have from Eq. (23) that the leading term in the expression for the stress is the Gaussian term, and therefore we expect to have the same scaling behavior as in Eq. (26). What distinguishes non-Gaussian networks from purely Gaussian ones is the nonvanishing elastic constants of the former. For percolation networks it is reasonable to assume that the elastic constants also follow a power law $C\sim(p-p_c)^g$. The elastic constants of a nearly Gaussian network should be ''almost'' zero, namely much smaller than the network stress. Therefore, the perturbative analysis in Sec. III would be self-consistent only if it yields that the exponent $g>f$. We can use expression (25) for the elastic constants to derive exact bounds on the value of the exponent g. Consider a percolation network of linear size L in d dimensions at p_c. An upper bound on the exponent g is obtained by including only a partial set of the bonds of the spanning cluster in the sum in expression (25). We take the set of singly connected bonds (SCBs), which are such bonds that removal of each one of them disconnects the spanning cluster. Their number scales as $L^{1/\nu}$ [22]. The force acting on a SCB is the total force applied on the surface of the system, which is proportional to $PL^{(d-1)}\sim L^{(-t/\nu+d-1)}$. The length to which a SCB is stretched, $(R_{\rm SCB})_0$, is proportional to the force, and therefore has the same scaling form

$$(R_{\rm SCB})_0\sim L^{(-t/\nu+d-1)}, \tag{27}$$

and consequently from Eq. (25) we get

$$C\sim L^{-g/\nu}\geqslant L^{-d}L^{1/\nu}L^{4(-t/\nu+d-1)},$$

which yields the upper bound $g\leqslant(4t-1)-\nu(3d-4)$. A lower bound for g is obtained by noting that for any bond other than the SCBs, $(R_{\rm bond})_0<(R_{\rm SCB})_0$. That is because the SCBs are the only bonds which experience the total force acting on the system. We use this fact in expression (25) and write that

$$C\sim L^{-g/\nu}\leqslant[(R_{\rm SCB})_0]^2\left\{\frac{1}{V}\sum_{\rm bonds}a[(R_{\rm bond})_0]^2\right\}.$$

The term in braces in the above inequality is, however, proportional to the pressure [see Eq. (24)], which scales like $L^{-t/\nu}$. This, together with result (27), brings us to the lower bound $g\geqslant 3t-2\nu(d-1)$. Using the known values of the exponents t and ν [23,8], we find that in three dimensions $2.48\leqslant g\leqslant 2.6$. In six dimensions both bounds coincide to give $g=4$. This last result reflects the fact that in six dimensions essentially all the bonds that carry the force across the network are SCBs. In two dimensions we have the bounds $1.22\leqslant g\leqslant 1.52$. However, we must mention a special feature of the two-dimensional case which questions the validity of the ''nearly'' Gaussian model. The model assumes that the contribution of the quartic term to the spring energy is small compared to the quadratic term [Eq. (21)]. This happens only if the bond length satisfies

$$R_{\rm bond}\ll(K/a)^{1/2}. \tag{28}$$

The longest bonds in the network are the bonds that *inside a cell of size* ξ^d serve as SCB's. Close to p_c, their length scales like

$$R_{\rm bond}\sim\xi^{-t/\nu+(d-1)}\sim(p-p_c)^{t-\nu(d-1)}\equiv(p-p_c)^y.$$

In two dimensions the exponent $y<0$, which implies that the length of the SCBs diverges, and certainly does not satisfy criterion (28). The problem is not limited to the SCBs only, but is relevant to a larger fraction of the bonds, including the doubly connected bonds, triply connected bonds, and so on. It is difficult to predict, *a priori*, whether this observation should modify the results of the nearly Gaussian model from Sec. III. Note that we do not encounter such a problem for a dimensionality larger than two, where the exponent y is positive.

V. SUMMARY AND DISCUSSION

We have studied the elastic properties of phantom Gaussian and nearly Gaussian networks. For Gaussian networks, the stress and elastic constants were calculated exactly. We found that a characteristic feature of Gaussian networks is the vanishing of their elastic constants. This feature is both temperature and network-topology independent. We also proved the equality between the stress tensor of a Gaussian elastic network to the conductivity tensor of a resistor network, in which the conductance of each resistor is equal to the corresponding spring constant $K^{\alpha\beta}$. This result quantifies the somewhat vague statement about an analogy between elasticity of Gaussian networks to conductivity of resistors networks.

We have investigated the nonlinear correction to the elastic behavior by studying the properties of networks of springs whose energies include small quartic terms in addition to the leading quadratic (Gaussian) terms. While the stress tensor is still dominated by the contribution of the quadratic term, the elastic constants (which vanish in the Gaussian network) are solely due to the non-Gaussian correction. We calculated the elastic constants to the first order in perturbation theory.

Finally, we applied the results of both the Gaussian and the nearly Gaussian models to describe the elastic behavior of phantom percolation networks close to the percolation threshold. Obviously, the well-known result that the shear modulus follows the same scaling law, $\mu\sim(p-p_c)^t$, like the conductivity, was recovered. We made a prediction that the elastic constants also follow a scaling law $C\sim(p-p_c)^g$, with exponent $g>t$, and found bounds on the values of the exponent g.

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APPENDIX: THE CONDUCTIVITY TENSOR OF FINITE RESISTOR NETWORKS

We consider a network whose bonds are resistors of conductance $K^{\alpha\beta}$, where the superscripts α and β label the nodes which the particular resistor connects. The network is finite and has an arbitrary topology, i.e., we make no assumption on the symmetry. We denote by $\vec{R}^{\beta}$ the position of the node β and by φ^{β} the electric potential at the node. The network is placed inside a rectangular box of volume $V = L_1 \times L_2 \times \cdots \times L_d$, where L_i is the length of the box along the ith Cartesian direction. (The derivation presented here can be easily generalized to systems of arbitrary shape.) The nodes of the network which are located on the surface of the system are called surface nodes, and we label them with the superscript s. The rest of the nodes are called the internal nodes, which we denote with the superscript α. The superscripts β and γ will be used to denote nodes of both types.

The conductivity of an electrical system is a tensor Σ_{ik} defined by

$$\langle j_i \rangle = \Sigma_{ik} \langle E_k \rangle, \tag{A1}$$

where the subscripts denote Cartesian coordinates and summation over repeated indices is implied, while $\langle \vec{j} \rangle$ and $\langle \vec{E} \rangle$ are the volume averages of the current density and the electric field, respectively. This definition of Σ_{ik} applies to continuous electrical systems. It can be generalized to discrete networks if we define the current density by a set of Dirac δ functions representing the currents in the bonds. Let us assume now that the electric potential φ, applied on the surface of the network, is such that on each surface point it is equal to the jth Cartesian coordinate of the point. Since $\vec{E} = -\vec{\nabla}\varphi$, we have

$$\begin{aligned}\langle E_k \rangle &= \frac{1}{V}\int E_k \, dV \\ &= -\int \frac{\partial \varphi}{\partial x_k} dV \\ &= \frac{1}{V}\left[-\int_{x_k = L_k} \varphi \, dS + \int_{x_k = 0} \varphi \, dS \right],\end{aligned}$$

where the surface integration is over the boundaries $x_k = 0$ and $x_k = L_k$, normal to the kth direction. However, with our choice for the electric potential on the boundaries, $\varphi = x_j$, it is easy to see that $\langle E_k \rangle = -\delta_{kj}$, where δ_{kj} is the Krönecker delta.

The mean current density $\langle j_i \rangle$ is given by

$$\langle j_i \rangle = \frac{1}{V}\int j_i \, dV. \tag{A2}$$

As we have already noted, the above definition (A2) applies to continuous electrical systems. To make it applicable to resistor networks we need to write the current density as a sum of Dirac δ functions representing the currents in the ''linear'' resistors. With this formal representation, the contribution to $\langle j_i \rangle$ of each resistor is given by the line integral

$$\int_{\vec{R}^{\alpha}}^{\vec{R}^{\beta}} I^{\alpha\beta} \, dx_i = K^{\alpha\beta}(\varphi^{\alpha} - \varphi^{\beta})(R_i^{\beta} - R_i^{\alpha}),$$

where $I^{\alpha\beta} = K^{\alpha\beta}(\varphi^{\alpha} - \varphi^{\beta})$ is the current across the resistor between nodes α and β. Adding the contributions of all the resistors we find that

$$\langle j_i \rangle = \frac{1}{V} \sum_{\langle \alpha\beta \rangle} K^{\alpha\beta}(\varphi^{\alpha} - \varphi^{\beta})(R_i^{\beta} - R_i^{\alpha}).$$

We may write the last result in a slightly different way

$$\begin{aligned}\langle j_i \rangle &= \frac{1}{2V}\left\{ \sum_{\gamma} \sum_{\beta} K^{\gamma\beta}\Theta^{\gamma\beta}(\varphi^{\gamma} - \varphi^{\beta})(-R_i^{\gamma}) \right. \\ &\qquad \left. + \sum_{\gamma} \sum_{\beta} K^{\gamma\beta}\Theta^{\gamma\beta}(\varphi^{\gamma} - \varphi^{\beta}) R_i^{\beta} \right\} \\ &= \frac{1}{V}\left\{ \sum_{\gamma} (-R_i^{\gamma}) \left[\sum_{\beta} K^{\gamma\beta}\Theta^{\gamma\beta}(\varphi^{\gamma} - \varphi^{\beta}) \right] \right\},\end{aligned}$$

where the variable $\Theta^{\gamma\beta}$ takes the value 1 if the nodes γ and β are connected by a resistor and if at least one of them is an internal node, and the value 0, otherwise. The sums in square brackets corresponding to internal nodes $\gamma = \alpha$ vanish due to the Kirchoff ''junction rule'' for the vanishing of the sum of currents entering an internal node,

$$\sum_{\beta} K^{\alpha\beta}\Theta^{\alpha\beta}(\varphi^{\alpha} - \varphi^{\beta}) = 0.$$

We are left with the contribution of the surface nodes $\gamma = s$ only, i.e.,

$$\langle j_i \rangle = \frac{1}{V}\left\{ \sum_{s} R_i^{s} \sum_{\beta} K^{\beta s}\Theta^{\beta s}(\varphi^{\beta} - \varphi^{s}) \right\}.$$

This last result can be also represented by summation over all the resistors $\langle \alpha s \rangle$, between surface and internal nodes

$$\langle j_i \rangle = \frac{1}{V}\left[\sum_{\langle \alpha s \rangle} K^{\alpha s} R_i^{s} (\varphi^{\alpha} - \varphi^{s}) \right].$$

Finally, since the electric field is equal to $\langle E_k \rangle = -\delta_{kj}$, we have from Eq. (A1) that

$$-\langle j_i \rangle = \Sigma_{ij} = \frac{1}{V}\left[\sum_{\langle \alpha s \rangle} K^{\alpha s} R_i^{s} (\varphi^{s} - \varphi^{\alpha}) \right].$$

We have obtained expression (19), which we constructed by mapping expression (15) for σ_{ij} into the electrostatic problem. This proves that indeed $\sigma_{ij} = \Sigma_{ij}$. Note that Σ_{ij} does not depend on the positions of the internal nodes but only on the details of the conductivity. In large random networks the relation (A1) suffices to define Σ_{ij} without need of a detailed specification of boundary conditions. However, our *exact* result is valid also for small networks of arbitrary topology, provided that the electric field $\vec{E}$ is generated using the very specific boundary conditions specified in the Appendix.

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