RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 3 1 AUGUST 1985

Superelastic percolation networks and the viscosity of gels

Muhammad Sahimi and Joe D. Goddard
Department of Chemical Engineering, University of Southern California, Los Angeles, California 90089-1211
(Received 22 April 1985)

We define a superelastic percolation network as one composed of Hookean bonds which take on infinite or unit spring constants with probabilities p and $1-p$, respectively. The elastic moduli of such networks diverge with an exponent τ as the elastic percolation threshold p_{ce} is approached from below. A homogeneous function representation of elastic moduli of percolation networks in the vicinity of p_{ce} is proposed. For a two-dimensional triangular network τ is estimated to be about 1.12 by phenomenological renormalization of Monte Carlo data. We suggest that the viscosity of gels, as p_{ce} is approached, may possibly diverge with exponent τ and not with the critical exponent of superconducting networks, as suggested by de Gennes.

There has recently been considerable interest in the problem of elastic properties of random networks near the percolation threshold. Until very recently this was mostly viewed as analogous to the problem of electrical conductivity of percolating networks. Thus de Gennes[1] pointed out that the bulk elastic modulus of a gel, modeled by a nonrotationally invariant isotropic force constant, is analogous to the electrical conductivity of the system. Feng and Sen[2] considered a different model, namely, the central force elastic percolating-network model, which is basically a network of simple springs that is rotationally invariant. Their numerical results indicate that this model may belong to a different universality class than the conductivity problem. A shortcoming of this model is the fact that for simple-cubic lattices *of any dimensionality* the elastic threshold is $p_{ce}=1$. Therefore, the study of this problem is limited to certain lattices such as triangular and fcc.

Another rotationally invariant model for the elastic moduli of percolating networks is the one in which *both* central and bond-bending forces are included. The potential energy of the network is given by

$$E=\frac{\alpha}{2}\sum_{\langle ij\rangle}[(\mathbf{u}_i-\mathbf{u}_j)\cdot\mathbf{e}_{ij}]^2 g_{ij}+\frac{\beta}{2}\sum_{\langle ijk\rangle}(\delta\theta_{ijk})^2 g_{ij}g_{ik}\ , \tag{1}$$

where $\mathbf{u}_i$ and $\mathbf{u}_j$ are displacements of sites i and j, and $\mathbf{e}_{ij}$ is a unit vector from site i to site j. g_{ij} is a random variable which takes the constant values b and a $(a<b)$ with probabilities p and $q=1-p$, respectively. The bond-bending forces between two occupied bonds ij and ik are given in terms of the change in angle $\delta\theta_{ijk}$ at site i, which is expressed in turn as a linear function of $\mathbf{u}_i$, $\mathbf{u}_j$, and $\mathbf{u}_k$. The sums are, respectively, over all bonds, and over all pairs having a site in common. α and β denote the stretching-force and the bond-bending force constants, respectively. This model has recently been studied extensively,[3-8] although its origin goes back many years.[9,10]

Before discussing the critical properties of elastic systems represented by (1), it is worthwhile to point out that the fundamental requirement of rotational, reflexional, and translational (Euclid) invariance of elastic energy[11,12] places severe restrictions on the admissible forms of series expansion of energy in terms of the nodal displacements in elastic networks. Of particular interest here are the quadratic terms, which determine the linear elasticity of such systems. Although invariance restrictions have been mentioned before,[2,3,5,6,8,11,12] it seems worthwhile to review them briefly as they relate to linear elasticity. The condition of translational invariance is satisfied automatically by adopting as independent variables the relative positions, $\mathbf{r}_I\equiv\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, where we use capital letters $I,\ldots$ to denote distinct pairs $(i,j),\ldots$. Then the condition of rotational invariance is satisfied by employing some appropriate subset of the various distinct scalar products of the relative positions, $q_\alpha=\mathbf{r}_I\cdot\mathbf{r}_J$, where we let Greek letters stand for distinct pairs $(I,J)\ldots$, and hence, for distinct quadruplets $(i,j,k,l),\ldots$

Under an orthogonal transformation of the system, defined by an orthogonal second-rank tensor $\underline{Q}$, we have

$$\mathbf{r}_I=\underline{Q}\cdot\mathbf{r}_I^0\ , \tag{2}$$

where $\underline{Q}^T=\underline{Q}^{-1}$. The q_α are invariant, and they provide a well-known integrity basis for rotationally invariant functions (1). Thus we can assume the elastic energy E is expressible uniquely as a function of the q_α and, given a perturbation $q_\alpha-q_\alpha^0$ from a base state q_α^0 (where $E\equiv 0$), E is given by

$$E=\sum_\alpha\left(\frac{\partial E}{\partial q_\alpha}\right)^0(q_\alpha-q_\alpha^0)+\tfrac{1}{2}\sum_\alpha\sum_\beta\left(\frac{\partial^2 E}{\partial q_\alpha\partial q_\beta}\right)^0(q_\alpha-q_\alpha^0)(q_\beta-q_\beta^0)+\cdots\ , \tag{3}$$

where the sums are taken over an appropriate subset of indices. If the base state is stable, then, by the usual arguments, the first sum in (3), which is linear in $q_\alpha-q_\alpha^0$, may be set equal to zero, and the quadratic term serves to define the linear elasticity.

The above representation is to be contrasted with that obtained by working directly in terms of the relative displacements $\mathbf{u}_I\equiv\mathbf{u}_{ij}=\mathbf{r}_I-\mathbf{r}_I^0$, which under (2) transform as

$$\mathbf{u}_I=\underline{L}\cdot\mathbf{r}_I^0\ , \tag{4}$$

with $\underline{L}=\underline{Q}-\underline{1}$. The general relation between the variables q and $\mathbf{u}$ is

$$q_\alpha-q_\alpha^0=\mathbf{r}_I^0\cdot\mathbf{u}_J+\mathbf{r}_J^0\cdot\mathbf{u}_I+\mathbf{u}_I\cdot\mathbf{u}_J\ , \tag{5}$$

the right side of which vanishes identically under the transformation (4), since

$$\underline{L}+\underline{L}^{T}+\underline{L}^{T}\underline{L}\equiv 0 \ . \tag{6}$$

However, if we had first substituted (5) into (3), regrouping terms according to whether they are linear or quadratic in $\mathbf{u}_l$, then the final terms on the right side of (5) would have been counted among the quadratic terms. This special type of quadratic term appears to correspond to the nonrotationally invariant elastic energy assumed by de Gennes[1] and more recently by Alexander.[3] While the latter attributes such terms to Born, it appears that the representation of Born and Huang[11] ultimately depends on a finite strain tensor having the form of the left side of (6) and exhibiting the correct invariance. Besides introducing spurious dependence of energy on rotation, we note that the splitting of the invariant form (5) into linear and quadratic terms in $\mathbf{u}$ may also generate a false stability criterion based on the linear terms in $\mathbf{u}$.

The constants a and b can be interpreted as the spring constants of two kinds of springs. Setting $a=0$ and $b=1$ results in the elastic percolation networks whose elastic moduli κ *vanish* as p_{ce} is approached *from above*: [3-8]

$$\kappa \sim (p-p_{ce})^{f} \ . \tag{7}$$

However, if we set $a=1$ and $b=\infty$, we obtain a percolating network of "soft" and "rigid" springs. For this network we expect that the elastic modulus κ *diverges* as p_{ce} is approached *from below,*

$$\kappa \sim (p_{ce}-p)^{-\tau} \ . \tag{8}$$

We call this a *superelastic* percolation network. This is similar to the percolation conductivity problem in which a conductor takes on the conductances b and a with probabilities p and q, respectively. For $a=0$ and $b=1$ the macroscopic conductivity σ of the network vanishes as $(p-p_c)^{t}$, whereas for $a=1$ and $b=\infty$, i.e., for a network of conductors and superconductors, σ diverges as $(p_c-p)^{-s}$. The problem of superconducting percolation networks has recently received considerable attention.[13-16] Here p_c, the percolation threshold of the network, is not necessarily the same as p_{ce}.[2-8]

Given the above considerations one may regard the point $a/b=0$ with $p=p_{ce}$ as a critical point for the elastic moduli of the system analogous to those studied in magnets and phase transitions (we assume that *all* elastic moduli vanish or diverge with the same exponent, f or τ). Thus, in translation from magnetic systems to elastic networks the variables temperature and field strength are replaced, respectively, by composition $\epsilon=p-p_{ce}$ and the ratio a/b. Similar statements can be made about percolation conductivity.[17] Therefore, one can construct a homogeneous-function representation for κ:

$$\kappa=\mu h(\epsilon\lambda^{-1}, a\mu^{-1}\lambda^{-\tau}, \mu b^{-1}\lambda^{-f}). \tag{9}$$

The homogeneous function h is defined whenever its three arguments are less than unity and it is singular if more than one argument vanishes. If the arguments of h remain within the domain of definition, then μ, which explicitly represents the invariance under scaling, may be chosen arbitrarily. If $a=0$, $b=b_1$, $\lambda=|\epsilon|$, and $\mu=\lambda^{f}b_1$, one obtains $\kappa=|\epsilon|^{f}b_1 h(1,0,1)$, whereas for $a=a_1$, $b=\infty$, $\lambda=|\epsilon|$, and $\mu=\lambda^{-\tau}a_1$, one has $\kappa=|\epsilon|^{-\tau}a_1 h(1,1,0)$. Therefore, Eq. (9) can properly represent κ and its vanishing or divergence at $\epsilon=0$, and it also suggests that f and τ are completely independent.

We now present an estimate of the exponent τ, which has not been estimated previously, and discuss its possible relevance to real systems. We have estimated τ for a triangular network. For percolation conductivity an exact duality relation yields $s=t$ in two dimensions; no such duality exists for the present problem. We have estimated τ by using a variant of finite-size scaling theory,[18] the so-called phenomenological renormalization (PR) of Monte Carlo data. Variants of this method have been already used in the study of critical phenomena,[19] although the treatment of data was different from the present method. For a network of linear dimension L one has[18]

$$\kappa \sim L^{\delta}h_1(L^{1/\nu_e}\epsilon) \ , \tag{10}$$

where for the present problem $\delta=\tau/\nu_e$ and ν_e is the correlation length exponent for the elastic percolation networks which is not necessarily the same as ν_p, the exponent of the usual percolation correlation length. In analogy with PR (Ref. 20) one infers a mapping $p\rightarrow p'$ via

$$\kappa_L(p)=(L/L')^{\delta}\kappa_{L'}(p') \ . \tag{11}$$

We now define

$$\zeta_{L,L'}=\ln[\kappa_L(p)/\kappa_{L'}(p)]/\ln(L/L') \ . \tag{12}$$

Then the intersection of $\zeta_{L,L'}(p)$ and $\zeta_{L',L''}(p)$ from *three sets of data* as a function of p is (p_{ce},δ). Once p_{ce} and δ are known, ν_e can be obtained from

$$(dp'/dp)_{p=p_{ce}}=(L/L')^{1/\nu_e} \ . \tag{13}$$

Therefore, although this method is similar in spirit to the PR of Nightingale,[20] it is different in detail. It is also more practical than the original PR from the point of view of Monte Carlo calculations, since the original PR method cannot be applied to three-dimensional systems at present. The advantage of the present method over the standard finite-size scaling method is that one does not need to know p_{ce} *a priori.* This method was recently used for three-dimensional percolation,[21] and the accuracy of the results, even with small to moderate values of L, was found to be comparable with those of the best available data.

For each network size enough independent realizations were made to reduce the standard deviations of the averaged quantities to a small value (no more than a few percent of the averages). This ranged from 1000 realizations for $L=8$ to 100 for $L=18$. The results are presented in Fig. 1 for $L=8$, $L'=12$, and $L''=18$. From this figure we obtain

$$p_{ce}\simeq 0.65 \ , \tag{14}$$

$$\tau/\nu_e\simeq 1.02 \ . \tag{15}$$

If we use Eq. (13) we obtain $\nu_e\simeq 1.1$, which means that $\tau\simeq 1.12$. We also carried out less extensive simulations with $L=12$, $L'=18$, and $L''=27$. The accuracy of the results were comparable with those of (14) and (15). The statistical errors of (14) and (15) are no more than those of the individual points of Fig. 1. Our result, $\nu_e\simeq 1.1$, is consistent with that of Lemieux, Breton, and Tremblay,[22]

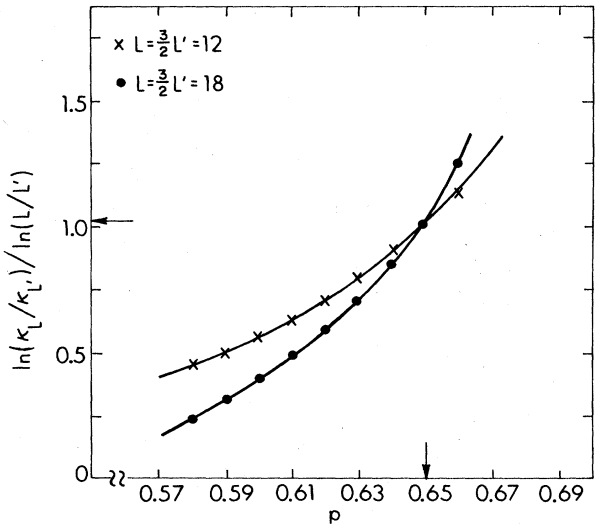

FIG. 1. Variations of the function $\zeta_{L,L'}=\ln(\kappa_L/\kappa_{L'})/\ln(L/L')$ against the fraction of superelastic springs p. Arrows indicate the locations of p_{ce} and δ.

$\nu_e \simeq 1.05 \pm 0.15$, and indicates that $\nu_e < \nu_p$ [where $\nu_p(d=2)=\frac{4}{3}$]. Our estimate of p_{ce} is in complete agreement with that of Lemieux *et al.*[22] These authors employed the transfer-matrix method and used up to 96 000 nodes to estimate f. If we use the same network sizes and the same method of estimation, we find $t/\nu_p \simeq 0.96$. This compares well with the most accurate estimate,[23] $t/\nu_p \simeq 0.973$. Thus, it appears that $f > \tau$ and $\tau < s$. We also note that the effective-medium approximation[24] is very accurate since it predicts that $\tau = 1$ and $p_{ce} = \frac{2}{3}$ for our system.

de Gennes[25] has suggested that the viscosity of gels, as the sol-gel transition point is approached, diverges with the critical exponent s described above. We believe that de Gennes's conjecture is not valid and suggest instead that the viscosity of gels may diverge with exponent τ introduced here. There are two reasons for our belief. First, the field equations for conductivity of percolation networks and the viscosity are totally different. Second, the published experimental data[26] on viscosity consistently yield exponents that are slightly smaller than s. This is consistent with our result that $\tau < s$, but close to it. It would be of great interest to calculate τ for a three-dimensional system, or for a continuum elastic percolation system, and to compare the result with the available data on viscosity to settle this issue. We hope to report the results of such a study in a future paper.

After the completion of this paper we received the report of a paper by Feng[27] in which he also discusses the concept of a superelastic percolation network. He studies the elastic properties of a two-dimensional system which is rotationally invariant. This model, the granular (or "disk") model, was introduced by Schwartz, Johnson, and Feng[28] in studying the vibrational properties of granular rocks. Feng[27] employs the nodes-links-blobs model of percolation backbones to argue that τ and s should be close to each other. By using numerical simulations and the standard finite-size scaling method, he estimates that $\tau(d=2) \simeq 1.02 \pm 0.07$, which is essentially consistent with our estimate. These results indicate that the critical exponents for *all* elastic systems may be the same, as long as important features of the model, such as rotational invariance and the absence of divergent inverse moments of the distribution of the elastic constants a and b, are preserved. Similar laws hold for the universality of the critical exponents of diffusion and conduction.[29]

This work was supported by a grant from the University of Southern California Faculty Research Innovation Fund to one of us (M.S.). We thank S. Feng for sending us a copy of his paper prior to publication.

[1]P. G. de Gennes, J. Phys. (Paris) Lett. **37**, L1 (1976).
[2]S. Feng and P. N. Sen, Phys. Rev. Lett. **52**, 216 (1984).
[3]Y. Kantor and I. Webman, Phys. Rev. Lett. **52**, 1891 (1984); S. Alexander, J. Phys. (Paris) Lett. **45**, 1939 (1984).
[4]L. Benguigui, Phys. Rev. Lett. **53**, 2028 (1984); D. Deptuck, J. P. Harrison, and P. Zawadzki, *ibid.* **54**, 913 (1985).
[5]S. Feng, P. N. Sen, B. I. Halperin, and C. J. Lobb, Phys. Rev. B **30**, 5386 (1984).
[6]S. Feng and M. Sahimi, Phys. Rev. B **31**, 1671 (1985).
[7]D. J. Bergman, Phys. Rev. B **31**, 1696 (1985).
[8]I. Webman and G. S. Grest, Phys. Rev. B **31**, 1689 (1985).
[9]G. J. Kirkwood, J. Chem. Phys. **7**, 506 (1939).
[10]P. N. Keating, Phys. Rev. **152**, 774 (1966).
[11]M. Born and H. Huang, *Dynamical Theory of Crystal Lattices* (Oxford Univ. Press, New York, 1954).
[12]W. Jaunzemis, *Continuum Mechanics* (MacMillan, London, 1967).
[13]A. Coniglio and H. E. Stanley, Phys. Rev. Lett. **52**, 294 (1984); A. Bunde, A. Coniglio, D. C. Hong, and H. E. Stanley, J. Phys. A **18**, L137 (1985).
[14]J. Adler, A. Aharony, and D. Stauffer, J. Phys. A **18**, L129 (1985).
[15]M. Sahimi, J. Phys. A **18**, 1543 (1985); M. Sahimi and H. Siddiqui, *ibid.* (to be published).
[16]T. Ohtsuki and T. Keyes, J. Phys. A **17**, L559 (1984).
[17]J. P. Straley, J. Phys. C **9**, 783 (1976).
[18]M. E. Fisher, in *Critical Phenomena, Proceedings of the International School of Physics, Enrico Fermi Course LI,* edited by M. S. Green (Academic, New York, 1971); M. N. Barber and W. Selke, J. Phys. A **15**, L617 (1982).
[19]W. Kinzel and J. M. Yeomans, J. Phys. A **14**, L163 (1981); K. Binder, Phys. Rev. Lett. **47**, 693 (1981).
[20]M. P. Nightingale, Physica A **83**, 561 (1976); J. Appl. Phys. **53**, 7927 (1982).
[21]M. Sahimi, J. Phys. A (to be published).
[22]M. A. Lemieux, P. Breton, and A.-M. S. Tremblay, J. Phys. (Paris) Lett. **46**, L1 (1985).
[23]J. G. Zabolitzky, Phys. Rev. B **30**, 4077 (1984); H. J. Herrmann, B. Derrida, and J. Vannimenus, *ibid.* **30**, 4080 (1984); D. C. Hong, S. Havlin, H. J. Herrmann, and H. E. Stanley, *ibid.* **30**, 4083 (1984); R. Rammal, J. C. Angles d'Auriac, and A. Beniot, *ibid.* **30**, 4087 (1984); C. J. Lobb and D. J. Frank, *ibid.* **30**, 4090 (1984).
[24]G. R. Jerauld, Ph.D. thesis, University of Minnesota, 1985 (unpublished); S. Feng, M. F. Thorpe, and E. Garboczi, Phys. Rev. B **31**, 2761 (1985).
[25]P. G. de Gennes, J. Phys. (Paris) Lett. **40**, L197 (1979).
[26]B. Jouhier, C. Allain, B. Gauthier-Manuel, and E. Guyon, Ann. Isr. Phys. Soc. **5**, 101 (1983).
[27]S. Feng, Phys. Rev. B **32**, 510 (1985).
[28]L. M. Schwartz, D. L. Johnson, and S. Feng, Phys. Rev. Lett. **52**, 831 (1984).
[29]M. Sahimi, B. D. Hughes, L. E. Scriven, and H. T. Davis, J. Chem. Phys. **78**, 6849 (1983).