Mechanics of disordered solids. II. Percolation on elastic networks with bond-bending forces

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Bond and site percolation on two- and three-dimensional (3D) elastic and superelastic percolation networks with central and bond-bending (BB) forces are studied. We calculate the force distribution and show that, depending on the relative contributions of the central and BB forces, its shape can be unimodal or bimodal, both near and away from the percolation threshold p_c. The Poisson ratios of various 2D and 3D, isotropic and anisotropic BB models are calculated and are shown to take on negative values near p_c. Several experimental realizations of this peculiar property are given. We then analyze various experimental data on elastic and rheological properties of gel polymers near p_c. The scaling laws for elastic properties of gel polmers near p_c and their associated critical exponents f are divided into two groups. In one group are *physical gels* in which the contribution of BB forces to the elastic energy dominates that of central forces (CF's), and their scaling properties are described by the BB model, with $f \simeq 3.75$. In the second group are *chemical gels* in most of which CF's are dominant, with $f \simeq 2.1$. The scaling laws for the viscosity of a gelling solution near the gel point can also be divided into two groups. In one group are gelling solutions that are close to the Zimm regime. We propose that the scaling properties of the viscosity of such gels is analogous to the shear modulus of a *static* superelastic percolation network that diverges, as p_c is approached from below, with an exponent $\tau = \nu - \beta_p/2 \simeq 0.68$ in 3D, where ν and β_p are the critical exponents of the correlation length and the strength of percolation networks, respectively. In the second group are gelling solutions that are close to the Rouse limit. We propose that the scaling law for the divergence of the viscosity of such gels is the same as that of the shear modulus of a *dynamic* superelastic percolation network, with $\tau' = 2\tau \simeq 1.35$ in 3D.

I. INTRODUCTION

In paper I we studied percolation on elastic networks with central forces (CF's). In this paper we investigate elastic and superelastic percolation networks with both central and bond-bending (BB) forces, which we refer to as the BB model. As discussed in paper I, the main shortcoming of CF percolation networks is that their percolation thresholds p_{ce} are much larger than those of ordinary (scalar) percolation p_c. Thus, for $p_c \leq p \leq p_{ce}$, where p is the fraction of intact bonds, an elastic percolation network (EPN) with CF's is geometrically connected, but its elastic moduli G (shear, bulk, and Young's) are all zero. This peculiar property makes an EPN with only CF's a somewhat unrealistic model of disordered solids. If there are correlations between the intact bonds,[1] then, the percolation threshold of the EPN with CF's will be less than p_{ce}, but in order to reduce the percolation threshold of a correlated CF network and make it equal to p_c, one has to introduce infinitely long-range correlations between the intact bonds. In practice, however, it is difficult to envision such a network. Despite this, the study of CF networks is useful because they are the simplest model of vector percolation and many of their properties are qualitatively similar to those of EPN's with more complex elastic energy and microscopic force laws.

The main advantage of the BB model is that its percolation threshold can be the same as that of scalar percolation if the appropriate microscopic force laws between the sites of the network are used, and hence the model can be used for investigating mechanics of disordered solids such as polymers, ceramics, and powders. In the present paper, we study both elastic and superelastic percolation networks (SEPN's) with central and BB forces in both two and three dimensions (3D).

II. THE BOND-BENDING MODEL

In general, the elastic energy of any BB model is given by

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

where α and β are the central and BB force constants, respectively, $\mathbf{u}_i$ is the (infinitesimal) displacement of site i, $\mathbf{R}_{ij}$ is a unit vector from site i to site j, and e_{ij} is the elastic constant of the bond (spring) between i and j. Here $\langle jik \rangle$ indicates that the sum is over all triplets in which the bonds j—i and i—k form an angle whose vertex is at i. The first term in Eq. (1) represents the usual contribution of CF's (see paper I), while the second term is due to angle-changing or BB forces. The precise form of $\delta\theta_{jik}$ depends on how much microscopic detail one would like to include in the model. If bending of bonds that make 180° with one another (i.e., collinear bonds) is not allowed, then,

$$\delta\theta_{jik} = (\mathbf{u}_i - \mathbf{u}_j)\cdot\mathbf{R}_{ik} + (\mathbf{u}_i - \mathbf{u}_k)\cdot\mathbf{R}_{ij} . \tag{2}$$

We refer to this particular version of the BB model as the Kirkwood-Keating (KK) model.[2,3] If, however, the bending of collinear bonds is allowed, then[4,5]

$$\delta\theta_{jik}=\begin{cases}(\mathbf{u}_{ij}\times\mathbf{R}_{ij}-\mathbf{u}_{ik}\times\mathbf{R}_{ik})\cdot(\mathbf{R}_{ij}\times\mathbf{R}_{ik})/|\mathbf{R}_{ij}\times\mathbf{R}_{ik}|, & \mathbf{R}_{ij}\text{ not parallel to }\mathbf{R}_{ik},\\ |(\mathbf{u}_{ij}+\mathbf{u}_{ik})\times\mathbf{R}_{ij}|\ , & \mathbf{R}_{ij}\text{ parallel to }\mathbf{R}_{ik}\end{cases}, \tag{3}$$

where, $\mathbf{u}_{ij}=\mathbf{u}_i-\mathbf{u}_j$. For *all* 2D systems, Eq. (3) is simplified to

$$\delta\theta_{jik}=(\mathbf{u}_i-\mathbf{u}_j)\times\mathbf{R}_{ij}-(\mathbf{u}_i-\mathbf{u}_k)\times\mathbf{R}_{ik}\ . \tag{4}$$

We refer to this as the BB model.

Phillips and Thorpe[6,8,9] used a mean-field theory to predict that the bond percolation threshold $p_{\rm KK}^B$ of a d-dimensional KK model with the coordination number Z is given by

$$p_{\rm KK}^B\simeq(1/Z)[(d^2+d)/(2d-1)]\ . \tag{5}$$

On the other hand, for scalar percolation one has[7]

$$p_c^B\simeq(1/Z)[d/(d-1)]\ . \tag{6}$$

Thus, for 2D systems, $p_{\rm KK}^B=p_c^B\simeq 2/Z$. However, for 3D systems, Eq. (5) predicts that

$$p_{\rm KK}^B\simeq 2.4/Z\ , \tag{7}$$

whereas Eq. (6) yields $p_c^B\simeq 1.5/Z$. Equation (7) was confirmed by numerical simulations.[10]

The BB model in d dimensions, on the other hand, has the same percolation threshold as the scalar percolation if each site of the network interacts with at least $d(d-1)/2$ of its nearest neighbors. Elastic percolation networks with BB forces have been studied extensively[11–17] in 2D. The most accurate estimate of the critical exponent f defined by

$$G\sim(p-p_c)^f\ , \tag{8}$$

is[17] $f(d=2)\simeq 3.96$. Rigorous bounds, $1+\nu d<f<\nu(d_{\rm min}+d)$, were also proposed,[11,18] where $d_{\rm min}$ is the fractal dimension of the shortest path of a percolation cluster.[19] Thus, one has $\frac{11}{3}<f(d=2)<4.17$, and $3.64<f(d=3)<3.85$, where[20] $d_{\rm min}\simeq 1.13$ and 1.34 for $d=2$ and 3, respectively. Moreover, Sahimi,[15] and later Roux,[16] proposed that

$$f=t+2\nu\ , \tag{9}$$

where t is the critical exponent of conductivity of percolation networks. In 3D, only bond percolation has been studied with the result[21] $f\simeq 3.78\pm 0.09$.

Superelastic percolation networks[22] with BB forces have also been stuided[22–26] in 2D. Such networks were first proposed[22] for modeling of the apparent divergence of the viscosity η of a gelling solution near and below the gel point. The critical exponent τ for SEPN's is defined by

$$G\sim(p_c-p)^{-\tau}\ . \tag{10}$$

III. RESULTS FOR ELASTIC PERCOLATION NETWORKS

We determined the force distribution (FD) (Ref. 27) of EPN's with BB forces in both 2D and 3D. In 2D we used a square network of size $L=40$ and calculated the FD at $p=0.9$ and $p=p_c^B=0.5$ for various values of β/α using 300 realizations. Figure 1 shows the resulting FD's at $p=0.9$. Far from p_c^B the contributions of CF's totally dominate the elastic energy E, in which case we may expect a unimodal FD, similar to those presented in paper I. However, if we decrease β, holding α fixed, we actually make the bending of two bonds with respect to each other easier, which means that the contribution of BB forces to E increases. As can be seen in Fig. 1, for $\beta/\alpha=100$, the BB contributions are so small that the FD is essentially unimodal.

If we lower β/α to 0.04, both CF and BB contributions become important and the FD takes on a distinct bimodal shape. The appearance of the second (smaller) maximum in the FD, which is to the left of the larger maximum (due to CF's) is due to the BB forces, in agreement with what we discussed in paper I. Further decrease in β/α to 0.001 means that the BB contributions are so large that the CF contributions can be neglected and, therefore, we may expect the FD to take on a unimodal shape again (see Fig. 1). But the maximum in this unimodal FD (due to BB forces) is of a different nature than that in the unimodal FD found for $\beta/\alpha=100$. Figure 2 shows our results for $p=p_c^B=0.5$. At p_c^B, the BB contributions are always large than those of CF's and depend only weakly on the value of β/α. As a result, although the FD is bimodal, the magnitude of the maximum due to the BB forces is much larger than that of CF's. Lowering the value of β/α has the effect of bringing the bimodal distribution closer to a unimodal one. But the dependence of the FD's shape on β/α is now much weaker and, as a result, the bimodal shape persists for values of β/α as small as 0.001.

Next, we determined the FD for a cubic network. We used a network of size $L=12$ and 200 realizations, and calculated the FD for two values of β/α at $p=0.9$ and

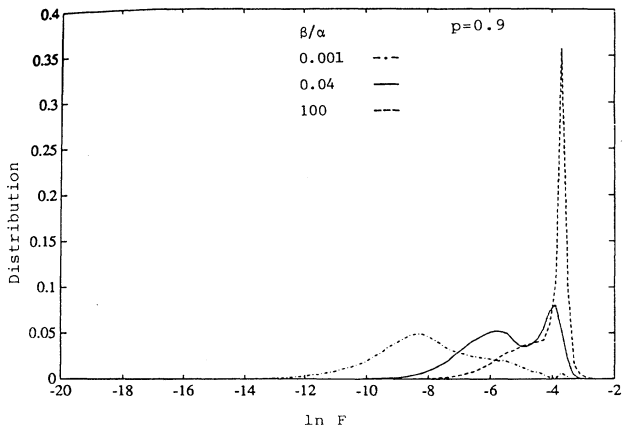

FIG. 1. Force distributions in the square network at $p=0.9$.

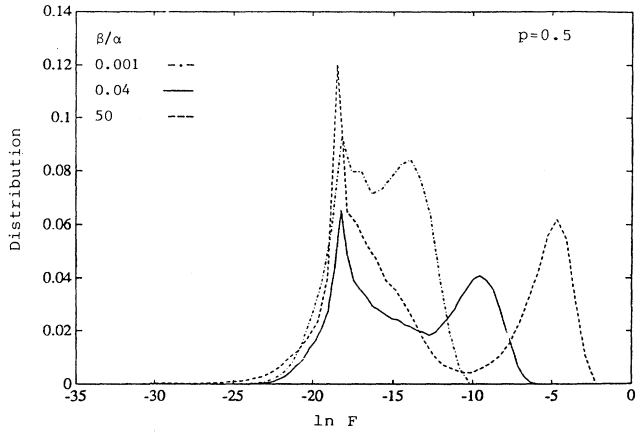

FIG. 2. Force distributions in the square network at $p_c^B=0.5$.

$p=p_c^B=0.249$. Figure 3 shows the resuslts for $p=p_c^B=0.249$. Consistent with the results for the square network, the FD at p_c^B is always bimodal and the magnitude of the maximum on the left side of the FD, which is due to BB forces, is much larger than that on the right side which is because of CF's. The results for $p=0.9$ are also qualitatively similar to those for the square network.

We also determined the moments $M(k)$ of the FD, for $k=0-4$, in the square and cubic networks at p_c^B. Table I shows the statistics of simulations. As in the case of the CF model, only percolating realizations were included in the statistics of Table I. To obtain precise estimates of $\hat{q}(k)$, the moments $M(k)$ were fitted to (see paper I)

$$M(k)\sim L^{-\hat{q}(k)}(a_1+a_2/\ln L+a_3/L)\ . \tag{11}$$

The resulting values of $\hat{q}(k)$ are shown in Table II. For the cubic network, the simulation results were too noisy to yield any reliable value of $\hat{q}(4)$. The estimated errors of $\hat{q}(k)$ are entirely statistical and do not include those due to finite-size effects, which can be quite large. For example, in the case of the square network, if we estimate $\hat{q}(2)$ from the 3 largest L's, we find $\hat{q}(2)\simeq 3.15$ and $\hat{q}(4)\simeq 11.2$. This value of $\hat{q}(2)$, which should be compared with $\hat{q}(2)\simeq 3.4$ obtained using all values of L used in the simulations, is much closer to $\hat{f}\simeq 3$, which is[17] the most accurate estimate of $\hat{f}$ and $\hat{q}(2)$ for 2D systems. However, within the estimated errors, they are consistent with one another. The values of $\hat{q}(0)$ agree nicely with the estimates of the fractal dimension $d_{\rm BB}$ of the backbone of percolation clusters, $d_{\rm BB}\simeq 1.64$ and 1.8 for $d=2$ and 3, respectively.

We can now compare the CF and BB models using the

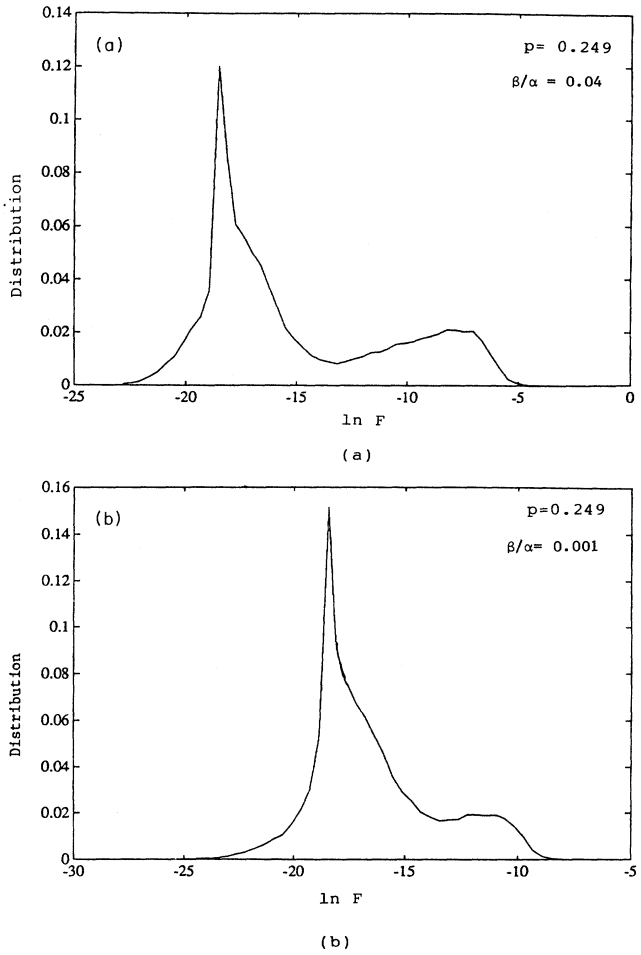

FIG. 3. Force distributions in the cubic network at $p_c^B=0.249$.

moments of their respective FD's as the basis of the comparison. A glance at Table II of this paper and Tables II and IV of paper I shows that for higher moments of the FD, the difference between the values of $\hat{q}(k)$ in the two models increases. This is because higher moments of the FD are affected more strongly by the fine details of the backbone, and the structures of the backbones of the two models are very different. The backbone in the CF model is dominated by multiply connected loops, whereas the backbone in the BB model can be well approximated by the relatively simple node-link blob model.[28] In this model, the backbone consists of a network of quasi-one-dimensional strings which are connected to one another

TABLE I. Number of percolating realizations for each network size L for calculation of the moments of the force distribution at the bond percolation threshold.

L	15	20	25	30	35	40	45	55
Square	1400	1000	1000	800	800	600	500	300
L	6	9	12	15	18	20		
Cubic	600	450	240	120	100	50		

TABLE II. Values of the exponents $\hat{q}(k)$ of the moments of the force distribution.

k	0	1	2	3	4
$\hat{q}(k)$ (square)	-1.65 ± 0.07	1.08 ± 0.8	3.4 ± 0.4	7.3 ± 0.9	11.3 ± 1.5
$\hat{q}(k)$ (cubic)	-1.9 ± 0.1	2.2 ± 0.2	4.6 ± 0.5	8.5 ± 1.3	

by nodes. Each string is supposed to consist of several sequences of singly connected bonds, in series with thicker blobs of multiple bonds. The fact that the values of $\hat{q}(1)$ in the two models are quite different provides further evidence for this, since the average force exerted on a bond of the backbone of the two models should be quite different.

We may draw a few conclusions from our study of the moments of the FD in the CF and BB models. First, since $M(1)$, the average force exerted on a bond, scales with the size of the system as $L^{-\hat{q}(1)}$, the torque m which is transmitted in a macrolink will be $m \sim M(1)\xi_p$, where ξ_p is the correlation length of percolation. Therefore, for a finite system of length L under an external stress σ, one must have $m \sim \sigma L^{-\hat{q}(1)+1}$. Hence the size dependence of the critical stress σ_c needed for *macroscopic* failure of the system is of a power-law type,[29] which is very different from its corresponding expression for the regime $p \approx 1$, which is[30] of the form $\ln L$. This will be further studied in paper III. Second, there appears to be no relation between the exponents of the FD of the BB model, in contrast with the CF model (see paper I), for which we found that there is a constant gap between $\hat{q}(k)$ and $\hat{q}(k+1)$. Finally, our study of the FD's of the CF and BB models show that, *at most* two moments of the FD of the two models, namely, $M(0)$ and $M(2)$, may have the same critical exponents. Therefore, we propose a general criterion for the universality of EPN's: In order that two elastic percolation models belong to the same universality class, *all moments of their FD's must have the same critical exponents.*

Our study of the CF model in paper I indicated that its scaling properties may be dependent on the type of percolation process (site, bond, etc). We thus investigated the universality of the critical properties of the BB model in 3D. In a previous paper,[2] we reported $f \simeq 3.78\pm0.09$ for the BB model in bond percolation on a cubic network. We thus estimated this exponent for site percolation on the same network. Table III presents the statistics of our simulations. We used finite-size scaling method and calculated the Young's modulus Y at $p_c^S \simeq 0.3116$ for various network sizes L. The results are shown in Fig. 4. Using an equation similar to (11) (in which $\hat{q}(2)=f/\nu$), we found $f/\nu \simeq 4.23\pm0.09$ which, together with $\nu(d=3) \simeq 0.88$, means that $f \simeq 3.72\pm0.08$, which is the same, within the numerical uncertainties, as that of bond percolation. Therefore, unlike the CF model, the BB model exhibits universal scaling properties. A simple arithmetic average of the two estimates yields

$$f \simeq 3.75\pm0.11 , \tag{12}$$

completely consistent with Eq. (9) which predicts that $f \simeq 3.76$. Limat[25] argued that Eq. (9) is *not* exact, because of the *eccentricity* E_c of elastic percolation clusters which measures the strength of a coupling effect between displacements and rotation that tends to rigidify the loops of the cluster. He suggested that $f=t+2\nu-\Delta$, where Δ is a new exponent which describes the scaling of E_c near p_c. Our 3D result, Eq. (12), indicates that $\Delta(d=3) \simeq 0.01$, while the 2D result[17] predicts that $\Delta(d=2) \simeq 0$. In the mean-field approximation which becomes exact for $d \geq 6$, one has $f=4$, $t=3$, and $n=\frac{1}{2}$ and thus $\Delta=0$. Therefore, $\Delta \simeq 0$ at *all* dimensions. This means that Ec may not be a critical quantity near p_c at all, or that near p_c one may have

$$E_c \sim \ln(p-p_c) , \tag{13}$$

so that $\Delta=0$.

TABLE III. Number of percolating realizations for each network size L for calculation of the elastic moduli of a cubic network at the percolation threshold.

L	6	9	12	15	18	20
Bond percolation	600	450	240	120	100	50
Site percolation	800	500	300	180	125	75

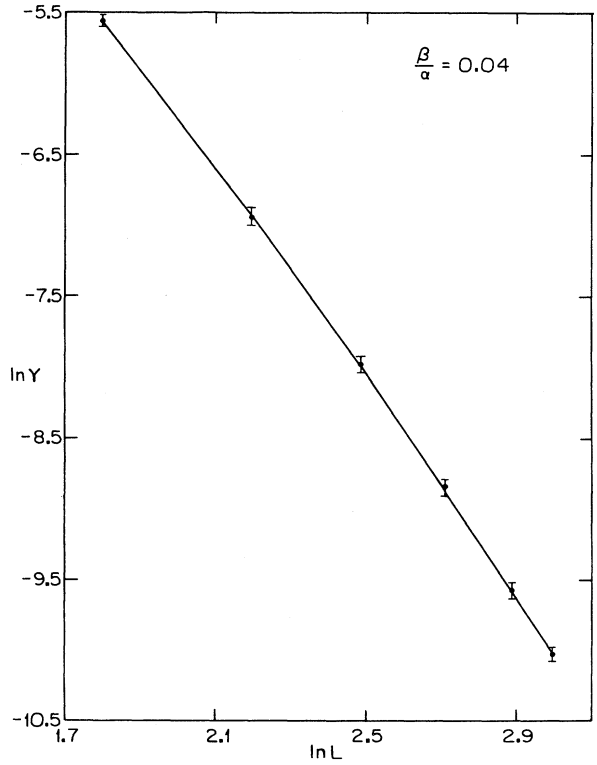

FIG. 4. Variations of the Young's modulus Y with the linear size L of the cubic network at $p_c^S=0.3116$.

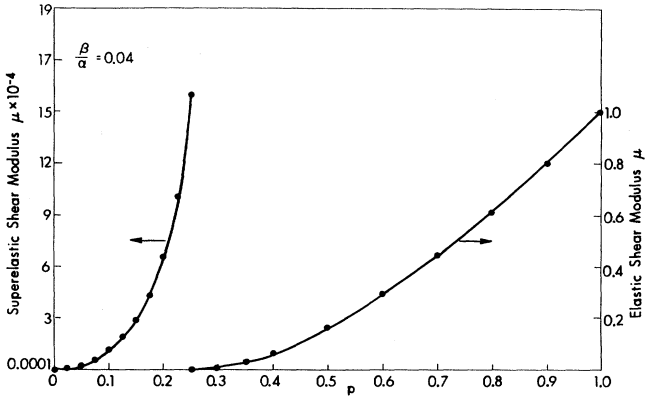

FIG. 5. Variations of the elastic and superelastic shear modulus μ with p in the cubic network. $p<0.249$ denotes the fraction of toally rigid bonds, while $p>0.249$ is the fraction of intact bonds.

IV. SUPERELASTIC PERCOLATION NETWORKS

In this section we report the results of our study of SEPN's with BB forces. Such systems can be thought of as a model of *random reinforcement* of disordered materials. Figure 5 shows the typical variations of the shear moduli of elastic and superelastic cubic networks. We investigated the scaling properties of SEPN's near p_c, and estimated the critical exponent τ defined by Eq. (10) using finite-size scaling analysis. For SEPN's, the contributions of the correction-to-scaling terms are even more important than those for EPN's discussed above. As discussed in paper I, in all of our analyses, we used various functional forms for the correction terms $g_1(L)$ and $g_2(L)$. To show the quality of the various fits using such functional forms, we show in Fig. 6 three different fits of the simulation results for the shear modulus μ of the cubic SEPN. The dotted curve was obtained using $g_1(L)=g_2(L)=0$, the dashed curve with

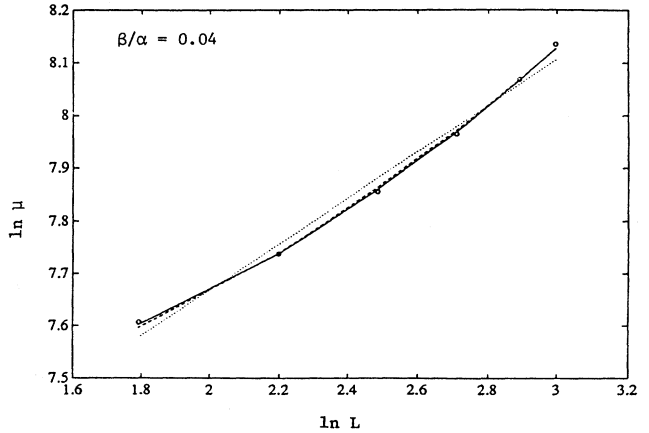

FIG. 6. Best fits of the simulation data obtained with various forms of correction-to-scaling terms g_1 and g_2. Dotted curve is for $g_1=g_2=0$, dashed curve for $g_1=(\ln cL)^{-1}$ and $g_2=L^{-1}$, and solid curve for $g_1=(\ln L)^{-1}$ and $g_2=L^{-1}$.

TABLE IV. Number of realizations for each network size L for calculation of the shear modulus of a superelastic percolation network at the bond percolation threshold.

L	15	20	25	30	35	40	50	60	70
Square	1500	1000	800	600	500	300	300	200	100
L	6	9	12	15	18	20			
Cubic	800	400	200	160	135	100			

$g_1(L)=(\ln cL)^{-1}$, and $g_2(L)=L^{-1}$, and the solid curve with $g_1(L)=(\ln L)^{-1}$, and $g_2(L)=L^{-1}$, where c is a constant. Clearly, the solid curve provides the most accurate fit to the data. Table IV presents the statistics of our simulations for both square and cubic networks. From these simulations we obtained

$$\tau\simeq 1.24\pm 0.03, \quad 2D\ , \tag{14}$$

$$\tau\simeq 0.65\pm 0.03, \quad 3D\ . \tag{15}$$

Both values are somewhat smaller than the corresponding values for the exponent s which characterizes the divergence of conductivity of *superconductive* percolation networks in which a fraction p of the bonds have *zero* resistance and the rest have a finite resistance,[31] $s(d=2)\simeq 1.2993\pm 0.0015$ and $s(d=3)\simeq 0.735\pm 0.005$. Earlier simulations,[22-24] which did not take into account the effect of correction to scaling, had not yielded a consistent estimate of τ in 2D: Sahimi and Goddard[22] and Feng[24] had reported that $\tau<s$, while Bergman[23] had claimed that $\tau=s$. Several authors[32,33] have suggested that

$$s=\nu-\beta_p/2\ , \tag{16}$$

where β_p is the critical exponent of the strength $P(p)$ of percolation networks defined by $P(p)\sim(p-p_c)^{\beta_p}$. However, the predictions of this equation do not agree with the numerical estimates of s mentioned above. Equation (16) predicts that in 2D (where $\nu=\frac{4}{3}$ and $\beta_p=\frac{5}{36}$), $s=\frac{91}{72}\simeq 1.264$, and in 3D (where $\nu\simeq 0.88$ and $\beta_p\simeq 0.41$), $s\simeq 0.675$. In our previous Letter,[26] we proposed that Eq. (16) is valid for the exponent τ and not s:

$$\tau=\nu-\beta_p/2\ . \tag{17}$$

The predictions of Eq. (17) agree with our estimates of τ given above. For one-dimensional systems, $\tau=1$, $\nu=1$, $\beta_p=0$, and in the mean-field approximation, valid for $d\geq 6$, $\tau=0$, $\nu=\frac{1}{2}$, and $\beta_p=1$, which again agree with Eq. (17). Thus, Eq. (17) might be exact in *all* dimensions, $1\leq d\leq 6$. Limat[34] proposed that $\tau=s-\Delta_1$, where Δ_1 is the analog of the exponent Δ, defined above, for SEPN's, and estimated that Δ_1 can be as large as $s/5$, consistent with our results.

V. THE POISSON RATIO

An important characteristic of any solid is its Poisson ratio ν_p. For a 2D *isotropic* solid, ν_p is given by

$$\nu_p = 1 - 2\mu/C_{11} , \tag{18}$$

whereas for a 3D isotropic solid the corresponding equation is

$$\nu_p = \frac{3(K/\mu)-2}{2+6(K/\mu)} . \tag{19}$$

The definition of ν_p for an *anisotropic* solid is arbitrary. In this section we compute ν_p for isotropic and anisotropic EPN's and SEPN's with BB forces.

We first calculate and discuss ν_p for the triangular network in the BB model which is isotropic. Figure 7 shows the results for both elastic and superelastic triangular networks of size $L=40$. While ν_p remains essentially constant in the elastic network as p, the fraction of intact bonds, is varied, it has a peculiar behavior in the superelastic triangular network as the fraction p of the totally rigid bonds approaches p_c. It reaches a minimum at about $p \simeq 0.05$, and then increases and achieves its maximum at about $p=0.1$. For $p>0.1$, it decreases monotonically and approaches a value $\nu_p \simeq -0.6$ at p_c. We have no explanation for this peculiar behavior of ν_p, since $p=0.05$ and 0.1 are not associated with any significant geometrical changes in the shape of the rigid clusters in a SEPN. Negative values of ν_p, which were also observed in the simulation of the BB model on a honeycomb network,[23] are intriguing, since isotropic materials with negative Poisson ratios are not common, although theoretically one can have highly compressible isotropic materials with Poisson ratios as low as -1. We can, however, mention some isotropic materials that do have a negative Poisson ratio. There are some manufactured foams[35] that are isotropic and their Poisson ratio is as low as -0.5. Data from the U.S. Bureau of Reclamation indicate that there are some rocks which have slightly negative values of ν_p, such as a sample of schist (sercite) with $\nu_p=-0.02$, phyllite (quatoze) with $\nu_p=-0.03$, and samples of granite with $\nu_p=-0.04$ and -0.10.

Next, we calculate ν_p for the cubic network which is anisotropic. This anisotropy makes the definition of ν_p somewhat arbitrary and direction dependent. We used a definition for an *effective* Poisson ratio due to Kittinger, Tich'y, and Bertagnoll:[36] Consider a Cartesian coordinate system x_1', x_2' and x_3' with axes parallel to the edges of a bar and with x_3' taken as the length direction, rotated with respect to x_1, x_2, and x_3. A generalized Poisson ratio for two specific transverse directions may be defined for an arbitrary lateral direction. This means that it can be given as a function of an azimuthal angle ϕ in the $x_1'x_2'$ plane, describing an arbitrary rotation about x_3'. The effective Poisson ratio ν_p' is defined by[36]

$$\nu_p' = -(S_{13}' + S_{23}')/(2S_{33}') . \tag{20}$$

The quantities S_{13}', S_{23}' and S_{33}' can be given in terms of the entries of the compliance tensor S discussed in paper I. For a cubic network, they are given by

$$S_{13}' = S_{12} , \tag{21}$$

$$S_{23}' = S_{12}(\cos^4\phi + \sin^4\phi) + 2(S_{11} - S_{44})\cos^2\phi \sin^2\phi , \tag{22}$$

$$S_{33}' = S_{11}(\cos^4\phi + \sin^4\phi) + (2S_{12} + S_4)\cos^2\phi \sin^2\phi . \tag{23}$$

If we substitute these into Eq. (20), after some manipulations we obtain

$$\nu_p' = -(A + B\cos 4\phi)/(C + D\cos 4\phi) , \tag{24}$$

where

$$A = 14S_{12} + 2S_{11} - S_{44} ,$$

$$B = 2S_{12} - 2S_{11} + S_{44} ,$$

$$C = 12S_{11} + 4S_{12} + 2S_{44} ,$$

$$D = 4S_{11} - 4S_{12} - 2S_{44} .$$

Note that for $\phi=0$ we recover the usual relation $\nu_p = -S_{12}/S_{11}$ for isotropic materials.

We now define an *average* effective Possion ratio $\langle \nu_p' \rangle$ by

$$\langle \nu_p' \rangle = \int_0^{\pi/2} \nu_p' d\phi , \tag{25}$$

which can be calculated analytically. To determine $\langle \nu_p' \rangle$ we need the compliances S_{11}, S_{12}, and S_{44} which, for a cubic network, are related to the elastic moduli by

$$S_{11} = \frac{C_{11}+C_{12}}{(C_{11}-C_{12})(C_{11}+2C_{12})} , \tag{26}$$

$$S_{12} = \frac{-C_{12}}{(C_{11}-C_{12})(C_{11}+2C_{12})} , \tag{27}$$

$$S_{44} = 1/C_{44} . \tag{28}$$

Therefore, we need to determine the elastic moduli C_{11}, C_{12}, and C_{44}. The elastic modulus C_{44} is the same as the shear modulus μ (see paper I) and is determined in the usual way. To calculate C_{11} we specify, as the boundary condition, a unit macroscopic strain on the top boundary of the cubic network in the *upward* direction. It is straightforward to show that the elastic modulus C_{12} can also be found from the *same* simulation (with the same boundary conditions) as that of C_{11}, by determining the sum of the forces that are exerted on one of the vertical planes of the network in the *horizontal* direction. This, however, necessitates the use of *free* boundary conditions

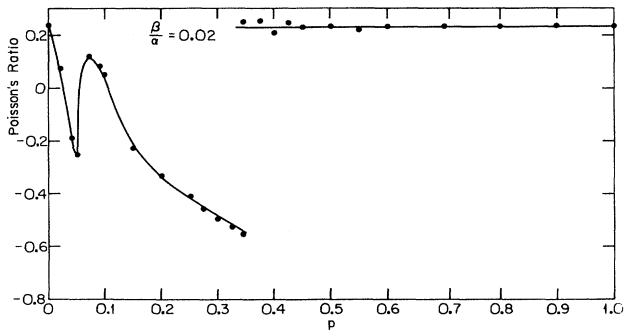

FIG. 7. Poisson ratio for elastic and superelastic triangular network. $p<0.347$ denotes the fraction of totally rigid bonds, while $p>0.347$ is the fraction of intact bonds.

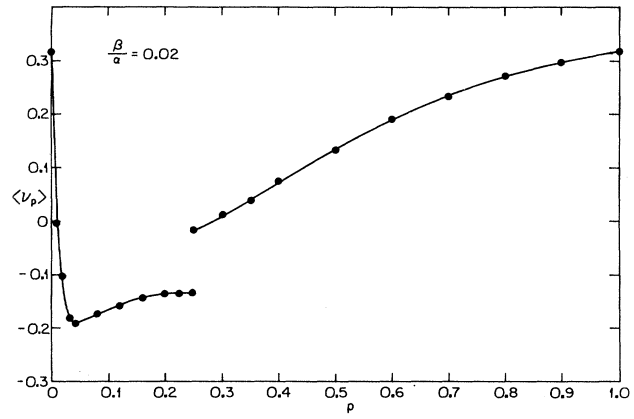

FIG. 8. Average Poisson ration $\langle \nu'_p \rangle$ for elastic and superelastic cubic network. p has the same meanings as in Fig. 5.

in the other two directions, instead of periodic boundary conditions that we have used so far.

We applied this method to both elastic and superelastic cubic networks. We used a network of size $L=12$, calculated the three elastic moduli C_{11}, C_{12}, and C_{44}, and determined $\langle \nu'_p \rangle$. Figure 8 shows typical results for $\beta/\alpha=0.02$. In the case of the elastic cubic network, $\langle \nu'_p \rangle$ is mostly positive, and its value decreases monotonically with p. It takes a slightly negative value near p_c. On the other hand, in the case of the superelastic cubic network, $\langle \nu'_p \rangle$ decreases sharply as p, the fraction of totally rigid bonds, increases, and reaches its minimum of about -0.2 at $p \simeq 0.03$, beyond which it increases again and reaches a value of about -0.13 at p_c. Love[37] presented an example of cubic *single-crystal* pyrite with a Poisson ratio of -0.14, and suggested that this effect may result from a twinned crystal. Evans and Caddack[38] demonstrated that microporous, anisotropic polytetrafluoroethylene has a large negative Poisson ratio, no matter how it is defined. We emphasize again that because of anisotropy of the cubic network, the Poisson ratio does not have a unique definition, and one can use alternative definitions for ν'_p. However, all sensible definitions of ν'_p would result in a $\langle \nu'_p \rangle$ whose typical behavior would be similar to Fig. 8. The conclusion is that negative Poisson ratios for anisotropic, and even isotropic, materials should not be considered as unphysical and, in fact, they may point to the possibility of designing a new class of materials with interesting and unusual properties. For example, they would have enhanced flexural rigidity and plane strain-fracture toughness, but lower bulk modulus K.

VI. COMPARISON WITH EXPERIMENTAL DATA

We now discuss the application of EPN's and SEPN's to the modeling of mechanical and rheological properties of disordered materials. Let us first summarize, in Table V, the critical exponents of various scalar and vector percolation models. The applicability of EPN's with BB forces for describing disordered solids such as powders is well known[39–42], and is not discussed here. Another class of materials to which elastic and superelastic percolation networks may be applicable are gel polymers. The scaling properties of the elastic moduli of gel polymers *above* and near the gel point, and those of the viscosity of a gelling solution *below* and close to the gel point have been controversial for several years. Numerous experimental measurements indicate that the viscosity η of a gelling solution below and near the gel point obeys the following scaling law

$$\eta \sim (\phi_c - \phi)^{-k} , \tag{29}$$

where ϕ is the gel fraction and ϕ_c its value at the gel point which is a percolation threshold. To compare the experimental results for the elasticity of gels with the predictions of EPN's, we first divide the gels into two groups. In the first group are what we call *physical gels,* in the formation of which chemical reactions play no role. Two examples are the gelation of silica particles in NaCl solutions and in pure water[43], and silica aerogels.[44] In such gels the BB forces are important since touching particles that form long chains, when deformed, roll on top of one another and this motion, together with the displacement of the centers of any three mutually touching particles, create forces that are similar to BB forces. Experimental measurements[43,44] of f for such gels confirm this: f is found to be about 3.8, in excellent agreement

TABLE V. Values of the critical exponents of scalar and vector percolation in d dimensions. Values of f and τ for the CF model refer to bond percolation. Values of t and s are independent of the model.

d	t/ν	s/ν	f/ν	τ/ν	Model
2	0.9745±0.0015	0.9745±0.0015	2.97±0.03	0.92±0.03	BB
			2.95±0.25	0.92±0.02	CF
3	2.27±0.01	0.835±0.005	4.3±0.1	0.74±0.04	BB
			2.1±0.2	0.80±0.03	CF
≥6	6	0	8	0	BB
			?	0	CF

with (12).

In the second group are what we call *chemical gels,* which are the usual branched polymers formed by a chemical reaction between the monomers. In most chemical gels BB forces are usually not important and the only important force between the monomers seems to be the CF's. There are numerous experimental measurements of f for such gels. Examples include measurement of f for hydrolyzed polyacrylamide,[45] and for tetraethylorthosilicate reactions.[46] These measurements have yielded a value of f in the range 1.9–2.2, which does not agree with the exponent of the BB model, but agrees nicely with the exponent of the 3D CF model, $f \simeq 2.1$. Although this value of f has been interpreted[47] in terms of an analogy between the elasticity and conductivity of percolation networks, we believe that this analogy is wrong. There is no justification for making an analogy between the elastic moduli and conductivity of percolation networks in order to estimate f, when we can directly obtain f by simulating EPN's instead of a random resistor network. Thus, our results for f in paper I and in this paper can be summarized as follows: for 3D systems $f \simeq 3.75$, if the contribution of BB forces dominates that of CF's (physical gels), while $f \simeq 2.1$ if the reverse is true (chemical gels). Alexander[48] argued that in some gels and rubbers which are under *internal* or *external* stress, there are terms in the elastic energy of the system which are similar to the Born model, the elastic energy of which is given by

$$E = \left[\frac{1+\nu_p}{1-\nu_p} \right] \sum_{\langle ij \rangle} [(\mathbf{u}_i - \mathbf{u}_j)\cdot \mathbf{R}_{ij}]^2 e_{ij} + \frac{1-3\nu_p}{4(1-\nu_p)} \sum_{\langle ij \rangle} (\mathbf{u}_i - \mathbf{u}_j)^2 e_{ij} \ . \tag{30}$$

In 3D the critical exponent of this system is $f = t \simeq 2$, because near p_c the contribution of the second term of the right-hand side of Eq. (30), which is a purely scalar term, dominates that of the first term (which is due to the CF's). However, because such rubbers and gels differ from the Born model in several important ways, such as the presence of nonlinear terms in their elastic energy, and the possibility of negative as well as positive Born coefficients (e.g., for $\nu_p > \frac{1}{3}$), it is not clear that the result $f = t$ is applicable to such systems. We should also mention that there are some chemical gels in which BB forces seem to be important and, thus, their scaling behavior is described by the BB model. An example is the result of Adam, Delsanti and Durand[49] for polycondensation, $f \simeq 3.3 \pm 0.5$. We must also point out that in some polymers entropic effects are important, whereas in our simulations such effects cannot be taken into account. It is not clear that, when such effects are taken into account, the critical exponent f would remain the same as those we find with our EPN's. Daoud and Coniglio[50] suggested that for such systems $f = \nu d$. For 3D systems this predicts, $f \simeq 2.64$, which is quite different from the exponents of CF and BB models. Whether the Daoud-Coniglio relation is exact and how the crossovers between these various regimes take place remain for a future study.

How can we explain the experimental data on the scaling behavior of η near the gel point? To begin with, we proposed that[26] the scaling properties of η near the gel point is analogous to that of the shear modulus μ of a SEPN near p_c. The *relation* between η and the shear modulus of an appropriate system can be inferred, in a straightforward and *rigorous* way, from the continuum equations of elasticity.[51] The *analogy* between η and the shear modulus of a SEPN is made simply because they both diverge as p_c and the gel point are approached. Similar to the case of the elastic moduli, we believe that the analogy between η and the conductivity of a superconducting percolation network[52,53] is inappropriate. However, even the analogy between η and μ is not nearly enough to explain the scaling of η near the gel point since experimental data indicate that the value of k is either in the range 0.6–0.8, or in the range[54] 1.3–1.5, whereas the shear modulus of a 3D SEPN is characterized by a *unique* value of τ given by Eqs. (15) and (17). The reason for having two distinct values of k is[26] that the dynamics of the two systems are totally different. In one case, the system is presumably close to the Zimm limit in which there is little or no polymer diffusion in the reaction bath, because of the strong hydrodynamic interactions between the monomers, and also between polymers of various sizes. Hence a SEPN, which is *static* system with fixed rigid clusters, may be suitable for simulating the Zimm regime. Indeed, our estimate of τ for such a system, $\tau \simeq 0.65$, supports the idea that those gelling solutions whose value of k is in the range 0.6–0.8, are in fact close to the Zimm regime.

On the other hand, the gelling solution can also be near the Rouse regime in which there are no hydrodynamic interactions between the polymers of various sizes and, therefore, the polymers can diffuse essentially freely in the reaction bath. To simulate this regime we proposed[26] a *dynamic* SEPN in which each cluster of totally rigid bonds represents a polymer, and there is of course a wide distribution of such polymers or clusters in the network. The soft bonds (those for which the elastic constant e is finite) represent the liquid (solution) medium in which the rigid clusters move randomly, with equal probability, in one principal direction of the network. This simulates the diffusion of the polymers in the reaction bath. Two rigid clusters cannot overlap, but they can temporarily join and form a larger cluster, which can be broken up again at a later time. We showed[26] that the shear modulus of this dynamic SEPN diverges with an exponent τ' given by

$$\tau' = 2\nu - \beta_p \ , \tag{31}$$

which, in 3D, predicts that $\tau' \simeq 1.35$, supporting the idea that those gelling solutions whose values of k are in the range 1.3–1.5 are close to the Rouse limit.

We should remark about some experimentally observed deviations of k from τ and τ'. Experimental determination of k and f involves measuring the complex shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ at a frequency ω,

where G' and G'' are the storage and loss shear moduli, respectively. At the gel point, G' and G'' are predicted to scale with ω as $G' \sim G'' \sim \omega^{\delta}$, where $\delta = f/(f+k)$. Strictly speaking, the scaling laws proposed here are valid only in the limit of $\omega \to 0$, whereas in practice it is highly difficult to achieve such a limit and, therefore, the reported values of k show some deviations from τ or τ'. However, we believe that such deviations are transient effects which should diminish as lower frequencies are achieved.

Finally, EPN's can be used for calculating compressional and shear wave velocities in a porous medium, and their dependence on the porosity of the medium. The shear wave velocity V_p is given by

$$V_p = [(K + \tfrac{4}{3}\mu)/\rho]^{1/2} , \tag{32}$$

while the compressional wave velocity is given by

$$V_s = (\mu/\rho)^{1/2} , \tag{33}$$

where ρ is the total density. Therefore, EPN's can also be used for modeling of wave propagation in porous media.

VII. SUMMARY

In this paper we investigated the scaling properties of elastic and superelastic percolation networks with central and BB forces. The scaling properties of these systems in 3D seem to be very different from those of CF models studied in paper I. We analyzed the experimental data on mechanical and rheological properties of disordered solids, gel polymers, and gelling solutions, and showed that elastic and superelastic percolation models with central and BB forces, or their appropriate modifications, provide consistent explanations for all such data.

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