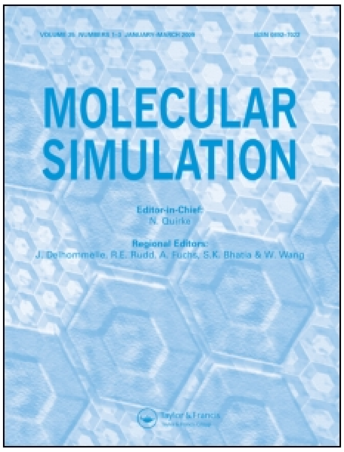
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Large Scale Computer Simulations of Static and Dynamic Properties of Disordered Materials

Sepehr Arbabi[a b]; Muhammad Sahimi[a]
[a] Department of Chemical Engineering, University of Southern California, Los Angeles, CA, USA [b] Reservior Engineering Research Institute, Palo Alto, CA

To cite this Article Arbabi, Sepehr and Sahimi, Muhammad(1991) 'Large Scale Computer Simulations of Static and Dynamic Properties of Disordered Materials', Molecular Simulation, 8: 1, 1 — 22

To link to this Article: DOI: 10.1080/08927029108022465

URL: http://dx.doi.org/10.1080/08927029108022465

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1991, Vol. 8, pp. 1–22
Reprints available directly from the publisher
Photocopying permitted by license only

LARGE SCALE COMPUTER SIMULATIONS OF STATIC AND DYNAMIC PROPERTIES OF DISORDERED MATERIALS

SEPEHR ARBABI* and MUHAMMAD SAHIMI**

Department of Chemical Engineering, University of Southern California, Los Angeles, CA 90089-1211, USA

(*Received December 1990, accepted April 1991*)

We have developed a unified approach for studying of morphological, mechanical and rheological properties of a large class of materials, including gel polymers and composite solids such as powders, colloidal aggregates and glassy networks. Our approach, which is based on an appropriate elastic or superelastic percolation network in which each bond represents an elastic element which can be stretched and/or bent, demonstrates clearly the fundamental role that the connectivity and various forms of deformation play in determining various properties of such materials. Moreover, our models reveal the existence of universal scaling laws for mechanical and rheological properties of such materials near a critical or phase transition point. In particular, we use our models to explain the phase transition that takes place in glassy networks, from a polymeric glass to an amorphous solid, in terms of a percolation model, and the experimentally-observed scaling laws for the viscosity of a gelling solution below and near a gelation point and the elastic moduli of gel polymers above and near the gelation point. In all cases, our results provide a consistent explanation for the experimental data.

KEY WORDS: Percolation, elastic energy, scaling laws, critical exponents, glassy networks, gel polymers, composite solids.

1 INTRODUCTION

The prediction of transport and mechanical properties of disordered solids is a task of both great difficulty and technological interest. Much of the difficulty is due to the subtle way in which the local morphology of a solid matrix influences its bulk behavior. The morphology of any disordered system has two aspects: geometry and topology. The geometry of a disordered medium describes the shapes and sizes of different microscopic elements or inclusions of the system. For example, in a porous medium the geometry describes the shapes and sizes of the pores. The topology of the system is the way the inclusions or elements are connected to one another.

Any fruitful attempt for determining transport and mechanics of disordered media has to include, as a first step, a realistic model of the disordered system. Many models have been proposed in the past, most of which have been too simple to realistically represent both the geometry and the topology of disordered systems. These include the bundle of pores model for describing porous media, and the spatially-periodic model for describing disordered solids. None of these can represent the topology of the kind of disordered systems that we are interested in here, e.g., gel polymer

---

*Present address: Reservoir Engineering Research Institute, 845 Page Mill Road, Palo Alto, CA 94304.
**Author to whom all correspondence should be addressed.

networks, colloidal aggregates and various glasses, which are made of networks of highly interconnected elements (atoms, monomers, etc.). Another approach has been to totally bypass this issue, and use average macroscopic continuum equations in which appear transport coefficients that have to be predetermined. This approach is phenomenological and provides no insight into how these coefficients depend on the morphology of the medium, unless careful experiments are carried out to determine this dependence.

In principle, any disordered system can be mapped onto an equivalent network of bonds and sites, in which bonds represent the elements of the system that transmit momentum, energy, stress, etc., and sites (in most cases) are massless points where bonds meet. That this can be done rigorously was shown by Mohanty [1]. The same type of networks can be obtained by discretization of the governing continuum equations of (scalar or vector) transport. Thus, network models represent a natural extension of continuum models. In the present paper, we use network models to represent a disordered material.

Suppose now that the bonds of the network have distributed properties, e.g., they represent channels of a porous medium, through which the flow of a fluid takes place, in which effective sizes (radii and lengths) are distributed according to statistical distributions, or that the bonds are springs to represent microscopic elements of a disordered solid, that can be stretched and/or bent, whose effective elastic constants are distributed according to a probability density function. Now, imagine that a fraction q of the bonds are *absent*, in the sense that they do not support the transport process, e.g., a channel of a porous medium has been plugged, or a spring has been cut so that there is a microcrack in the solid, or that a gel polymer network is near its gelation point (GP), so that it does not have a regular structure, as if some of its chemical bonds are missing. Such a structure is called a bond percolation network [2]. If q is large enough, no sample-spanning paths of *present* or intact bonds exists, and no macroscopic transport (of current, stress, etc.) takes place. On the other hand, if $q \approx 0$, the system is almost fully connected and macroscopic transport occurs. Thus, there must exist a critical value q_c of q, such that for $q > q_c$ no macroscopic transport takes place, and for $q \leqslant q_c$ the network can support macroscopic transport. In such a network, $p_c^B = 1 - q_c$ is called the bond percolation threshold of the system. Alternatively, one may imagine that a fraction q of the sites of the network and all bonds that are connected to such sites are absent. Then, one can define, in an analogous way, a site percolation threshold, p_c^S such that for $p = 1 - q < p_c^S$ the network can not support macroscopic transport. It is clear that the passage from a regime of no macroscopic transport to one in which there is macroscopic transport is because of the structural or geometrical phase transition that takes place at the percolation threshold. Table 1 gives the currently-accepted values of p_c^B and p_c^S for common two- and three-dimensional networks. Percolation networks have proven to be reasonable models for gel polymers [3], sintered powders [4], colloidal aggregates [5], porous media [6] and glasses [7].

So far, this description of percolation networks is abstract. Depending on a specific application, the bonds or sites of the network can take on certain physical meaning. For example, the bonds can represent linear or non-linear resistors with distributed resistivities or conductances. If a porous medium can be represented by a random network, then, it is not difficult to see that there is a one-to-one correspondence between the flow field in the porous medium, which can be linear as in the case of Newtonian fluids or non-linear as in the case of non-Newtonian fluids or turbulent

Table 1 Currently-accepted values of the (scalar) bond and site percolation thresholds for some common lattices in 2 and 3 dimensions.

$d = 2$	p_c^B	p_c^S
Honeycomb	$1 - 2 \sin (\pi/18) \simeq 0.6527$*	0.6962
Square	1/2*	0.5927
Triangular	$2 \sin (\pi/18) \simeq 0.3473$*	1/2*
$d = 3$	p_c^B	p_c^S
Diamond	0.3886	0.4299
Simple Cubic	0.2488	0.3116
BCC	0.1795	0.2464

* denotes an exact result.

flow, and the current in the random resistor network. Alternatively, if the network represents a disordered solid, one can establish a one-to-one correspondence between the flow of heat or electrical current in the solid and the current field in the network. We call this *scalar percolation*, since one is concerned with a scalar transport process in a percolation system. On the other hand, when bonds represent elastic elements (springs) that can be stretched and/or bent, we have an elastic percolation network (EPN) which, with various microscopic force laws, can take into account the vectorial nature of transport of stress in disordered solids. For the obvious reason, we call this *vector percolation*.

In this paper, mechanical, morphological and rheological properties of two classes of materials are studied. The first class includes gel polymers networks, sintered powders and colloidal aggregates. We are interested in the mechanical and rheological properties of such networks. The second class includes covalent networks and glasses. We are interested in their morphological properties. In particular, we demonstrate the fundamental role that the coordination number Z of such systems, i.e., the number of present or intact bonds connected to the same site, plays in determining their various properties. We show that a unified approach can be developed to study various properties of such materials.

The plan of this paper is as follows. In the next section we desribe the models that we employ in the paper to study various properties of the disordered materials mentioned above. In sections 3 and 4 we focus our attention on two specific systems. We first study, in section 3, percolation and connectivity effects in the formation of various glassy networks, using our models. Then, in section 4 we use our models to study elastic properties of gel polymer networks *above* the GP, and the viscosity of the gelling solution *below* the GP. In particular, we are interested in the behavior of the properties of the system in the vicinity of the GP. We show that in all cases our results provide consistent explanations for the available experimental data. The paper is summarized in section 5, where we also point out how our models and approach can be used to study more complex phenomena in disordered materials.

2 DISCRETE MICROSCOPIC MODELS OF DISORDERED MATERIALS

In this paper, the disordered system is represented by a three-dimensional network in which each bond represents an elastic element (spring) with an elastic constant e, which can take on values selected from a probability density function $F(e)$. We consider here the simplest case in which

$$F(e) = p\delta(e - a) + (1 - p)\delta(e - b), \tag{1}$$

i.e., e takes the value a and b with the probabilities p and $1 - p$, respectively. In a large enough network, this is equivalent to having a network in which a randomly-selected fraction p of the springs have an elastic constant a, whereas the remaining springs have an elastic constant b. More generally, we can replace $F(e)$ with, $F(e) = pf_1(e) + (1 - p)f_2(e)$, where f_1 and f_2 are two continuous (and normalized) probability density functions, but for the purpose of the present paper the above simple distribution suffices. If a is finite and $b = 0$, we obtain an EPN described above. In this case, as p decreases all elastic moduli of the network also decrease and eventually vanish at $p = p_e^B$, which is the *elastic* bond percolation threshold of the network. The value of p_e^B is not necessarily the same as p_c^B, the bond percolation threshold of the network defined above. The reason for this is that one may form networks of such springs which, although they are macroscopically connected, they do not support transport of stress, since their deformation might be done at no cost to the elastic energy of the system. Later in this section, we discuss condition(s) under which $p_e^B = p_c^B$. Another case of interest is when $a = \infty$ and b is finite, i.e., a fraction p of the springs are totally *rigid*, and the rest are *soft*. We call this a *superelastic percolation network* (SEPN). In this system, as p_e^B is approached from *below*, larger and larger islands of totally rigid springs are formed, as the result of which all elastic moduli of the network increase. At $p = p_c^B$, a sample-spanning cluster of totally rigid springs is formed and all elastic moduli of the network *diverge*. As we argue below, this system may be relevant to modeling of rheological properties of a gelling solution below the GP.

It remains to specify the microscopic force law that each spring of the system obeys. In principle, one can use any kind of microscopic law, but in the present paper we restrict our attention to a few models which we now describe. In the first model, the elastic energy of the network is given by

$$h = \left(\frac{1 + v}{1 - v}\right) \sum_{ij} [(\mathbf{u}_i - \mathbf{u}_j)\cdot\mathbf{R}_{ij}]^2 e_{ij} + \frac{1 - 3v}{4(1 - v)} \sum_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2 e_{ij} \tag{2}$$

where $\mathbf{u}_i$ and $\mathbf{u}_j$ are the (infinitesimal) displacements of sites i and j, $\mathbf{R}_{ij}$ a unit vector from site i to site j, e_{ij} the elastic constant of the bond (spring) between sites i and j, and v the Poisson's ratio. Theoretically, for *isotropic* materials the Poisson's ratio is in the range $-1 < v < 1/3$, but in practice one usually has $0 < v < 1/3$. The first term in Equation (2) represents the contribution of the stretching or central forces (CFs). Equation (2) describes the elastic energy of the so-called *Born model* [8]. Jerauld [9] showed that the above elastic energy can be obtained by discretizing the *Navier* equations. If a disordered system is described by the above elastic energy, then it can be shown that near p_c^B the contribution of the second term of Equation (2), which is essentially a *scalar* term (as oppposed to the first term which is a vectorial contribution), dominates the elastic energy H. Therefore, as long as $v \neq 1/3$, the elastic percolation threshold of the system is the same as p_c^B, since the contribution of the scalar term, which is completely due to the *connectivity* of the system, dominates H. The disadvantage of this model is that it *is not rotationally invariant* which is not realistic. This non-rotational invariance of the system is unexpected since the Navier equation, which is supposedly the continuum counterpart of the Born model, is of course rotationally invariant. Although the origin of this contradiction between the continuum model and its discrete counterpart is not completely clear yet, one may speculate that the discretization procedure can give rise to this unexpected behavior.

If $v = 1/3$, one obtains the CF model which is essentially a network of simple springs that can be stretched. It is easy to see that the CF model *is* rotationally invariant, and since there is no scalar contribution to the elastic energy of the CF model, one has $p_e^B \neq p_c^B$. In certain EPNs with only CFs, the problem of determining the elastic moduli of the network is trivial. For example, it can be shown that for the square and cubic networks with only CFs, $p_e^B = p_e^S = 1$, i.e., for any $p < 1$ all elastic moduli are zero. Thus, the CF model is restricted to certain networks whose connectivity and topological properties are complex enough that can give rise to non-zero elastic moduli by transmitting only CFs. Computer simulations show that [10, 11] for a triangular network ($Z = 6$), $p_e^B \simeq 0.642$, which should be compared with the exact value, $p_c^B = 2\sin(\pi/18) \simeq 0.347$, and [12] for a body-centered cubic (BCC) network, $p_e^B \simeq 0.737$, which should be compared with $p_c^B \simeq 0.195$. Thus, an EPN with only CFs is not a very realistic model for many disordered materials, since for $p_c^B < p < p_e^B$, one has an elastic network which, although macroscopically connected (since $p > p_c^B$), it has no non-zero elastic modulus. Despite this shortcoming, the CF model is a useful system to study, because it is the simplest EPN whose properties are qualitatively similar to those of EPNs with more complex energy and microscopic force laws described below. We should point that, determining p_e^B for any given system is much more difficult than p_c^B. Whereas numerical estimation of p_c^B only requires finding the smallest value for p for which the network is macroscopically connected (a purely topological problem), determining p_e^B requires the EPN to be not only macroscopically connected, but it must also have non-zero elastic moduli. Thus, in this latter case, one has to explicitly solve for the elastic moduli which requires large scale simulation (see below).

When deforming any EPN, one expects to not only stretch the bonds, but also change the angle between any pair of bonds that have one site in common. Thus, the elastic energy of the system should contain the contribution of both the CF and angle-changing or bond-bending (BB) forces. Hence, for such a system one should have

$$H = \frac{\alpha}{2}\sum_{ij}[(\mathbf{u}_i - \mathbf{u}_j)\cdot\mathbf{R}_{ij}]^2 e_{ij} + \frac{\beta}{2}\sum_{jik}(\delta\theta_{jik})^2 e_{ij}e_{ik}, \tag{3}$$

where α and β are the stretching (CF) and BB force constants, respectively. The first term in Equation (3) represents the usual contribution of the CFs, while the second term represents the contribution of angle-changing or BB forces which, for two bonds ij and ik, is written in terms of the change in the angle $\delta\theta_{jik}$ between the two bonds. The two sums in Equation (3) are, respectively, over all bonds and all pairs of bonds with a site i in common. The precise form of $\delta\theta_{jik}$ depends on how much microscopic details one includes in the model. If bending of bonds that make 180 degrees with one another is not allowed (i.e., the angle between colinear bonds does not change during deformation), then,

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

This model is essentially the same as that of Kirkwood [13] who studied the vibrational properties of rod-like molecules, and that of Keating [14] who investigated the elastic properties of covalent crystals. We refer to this model as the Kirkwood-

Keating (KK) model. If, however, the bending of colinear bonds is allowed, then,

$$\delta\theta_{ijk} = \begin{cases} (\mathbf{u}_{ij} \times \mathbf{R}_{ij} - \mathbf{u}_{ik} \times \mathbf{R}_{ik})\cdot(\mathbf{R}_{ij} \times \mathbf{R}_{ik})/|\mathbf{R}_{ij} \times \mathbf{R}_{ik}| & \mathbf{R}_{ij} \text{ not } \| \text{ to } \mathbf{R}_{ik}, \quad (5a) \\ |(\mathbf{u}_{ij} + \mathbf{u}_{ik}) \times \mathbf{R}_{ij}| & \mathbf{R}_{ij} \| \text{ to } \mathbf{R}_{ik}, \quad (5b) \end{cases}$$

where, $\mathbf{u}_{ij} = \mathbf{u}_i - \mathbf{u}_j$. In the special case of a cubic network in d dimensions, Equations (5) are simplified to

$$\delta\theta_{jik} = (\mathbf{u}_i - \mathbf{u}_j) \times \mathbf{R}_{ij} - (\mathbf{u}_i - \mathbf{u}_k) \times \mathbf{R}_{ik}. \qquad (6)$$

We refer to this system as the BB model.

Phillips and Thorpe [15] studied the percolation properties of the KK model. Using a mean-field argument, they proposed that for a d-dimensional KK model in a network of coordination number Z, one has

$$p_e^B \simeq \frac{1}{Z}[(d^2 + d)/(2d - 1)] \qquad \text{KK model} \qquad (7)$$

On the other hand, for scalar percolation in d dimensions one has [16]

$$p_c^B \simeq \frac{1}{Z}[d/(d - 1)] \qquad \text{scalar model} \qquad (8)$$

which means that for two-dimensional systems the elastic percolation threshold of the KK model and that of the scalar percolation are identical ($p_c^B = p_e^B \simeq 2/Z$). For three-dimensional systems, Equation (7) predicts that, $p_e^B \simeq 2.4/Z$, whereas for scalar percolation Equation (8) yields, $p_c^B \simeq 1.5/Z$, so that the KK and scalar percolation systems have different percolation thresholds for $d = 3$. The BB model, on the other hand, has the same percolation threshold as the scalar percolation if each site of the system interacts with at least $d(d - 1)/2$ of its nearest-neighbor nodes. For this reason, the BB model is the most general elastic percolation model since, by including enough microscopic details, one can force the elastic percolation threshold of the system to be identical with that of the scalar percolation. Jerauld [9] and Feng *et al.* [17] studied the CF model and derived the following formula

$$p_e^B \simeq 2d/Z \qquad \text{CF model} \qquad (9)$$

which correctly predicts, $p_e^B = 1$ for a d-dimensional cubic network ($Z = 2d$). Equation (9) also predicts that, $p_e^B = 2/3$ for the triangular network ($Z = 6$), and $p_e^B = 3/4$ for the BCC network ($Z = 8$), which are in close agreement with the numerical estimates mentioned above.

We can provide a geometrical interpretation of Equations (7)–(9). Since for any given p, the quantity pZ is the *average* coordination number $\bar{Z}$ of the network, Equation (7) predicts that at the elastic percolation threshold of the KK model, one has

$$\bar{Z} \simeq (d^2 + d)/(2d - 1) \qquad \text{KK model} \qquad (10)$$

whereas at the elastic threshold of the CF model, one obtains

$$\bar{Z} \simeq 2d \qquad \text{CF model} \qquad (11)$$

and at the percolation threshold of the scalar model, we have

$$\bar{Z} \simeq d/(d - 1) \qquad \text{scalar model} \qquad (12)$$

Equation (11) explains clearly why the CF model is a trivial problem on certain networks since, according to this equation, the coordination number of a d-dimensional network must be *greater* than $2d$ in order to have non-zero elastic moduli. This is why with only CFs honeycomb ($Z = 3$) and square ($Z = 4$) networks in two dimensions, and diamond ($Z = 4$) and cubic ($Z = 6$) networks in three dimensions do not have any non-zero shear modulus for any p, or Young's or bulk modulus for $p < 1$.

We now have completed the description of the models that we use to study various properties of disordered materials. In the next section, we describe the results of our large scale Monte Carlo (MC) calculations of such systems, and compare them with the relevant experimental data. But before closing this section, let us briefly discuss how the MC calculations are done. In order to calculate elastic properties of a given model, we minimize its elastic energy H with respect to the nodal displacement $\mathbf{u}_i$

$$\frac{\partial H}{\partial \mathbf{u}_i} = 0. \tag{13}$$

Writing down this equation for every interior node of the network results in a $3N$ simultaneous linear equations for nodel displacement $\mathbf{u}_i = (u_{ix}, u_{iy}, u_{iz})$ of a three-dimensional networks of N nodes. The boundary conditions depend on the quantity that we would like to calculate. For example, for the elastic constant C_{11} we stretch two opposite faces of the network by a given strain U_b, and impose periodic boundary conditions in the other directions. The resulting set of linear equations are solved by the adaptive accelerated Jacobi-conjugate gradient method, that uses an acceleration parameter which is optimized for each iteration. From the solution of the set for the nodal displacements we calculate the elastic energy H of the system, and, hence, the elastic modulus $C_{11} = 2H/U_b^2$. We use the same method to calculate the shear modulus κ, except that we shear the system in the transverse direction by an amount U_b. A similar method is used to calculate the Young's modulus. All of our computations were carried out on Crays X-MP and Y-MP of the San Diego Supercomputer Center. Network sizes ranging from $L = 6$ to $L = 20$ were used. For each network size, enough independent realizations were made to insure that the average of the results over all realizations did not change significantly if more realizations were made. Thus, the number of realizations varied from about 1500 for the smallest network to 50 for the largest one, and we used the BCC and cubic networks. For the $L = 20$ cubic network, one has to solve about 22,000 linear equations for *each* realization, which is one of the largest simulations of its kind for percolation systems.

3 MORPHOLOGICAL PROPERTIES OF GLASSY NETWORKS

Microscopic topology plays a fundamental role in the properties of glass-forming components, and its role has been studied theoretically and experimentally for many years. The first influential paper in this area was perhaps that of Zachariasen who studied the SiO_2 system nearly 60 years ago and stated bluntly that, "it must be frankly admitted that we know practically nothing about the atomic arrangement in glasses". Phillips [18] introduced the concept of an average atomic coordination number in order to explain the strong glass-forming tendency of certain alloy composition. Phillips proposed that the glass-forming condition is in the form, $N_{\mathrm{con}} = N_d$, where N_{con} is the number of interatomic force-field constraints, and N_d the number of

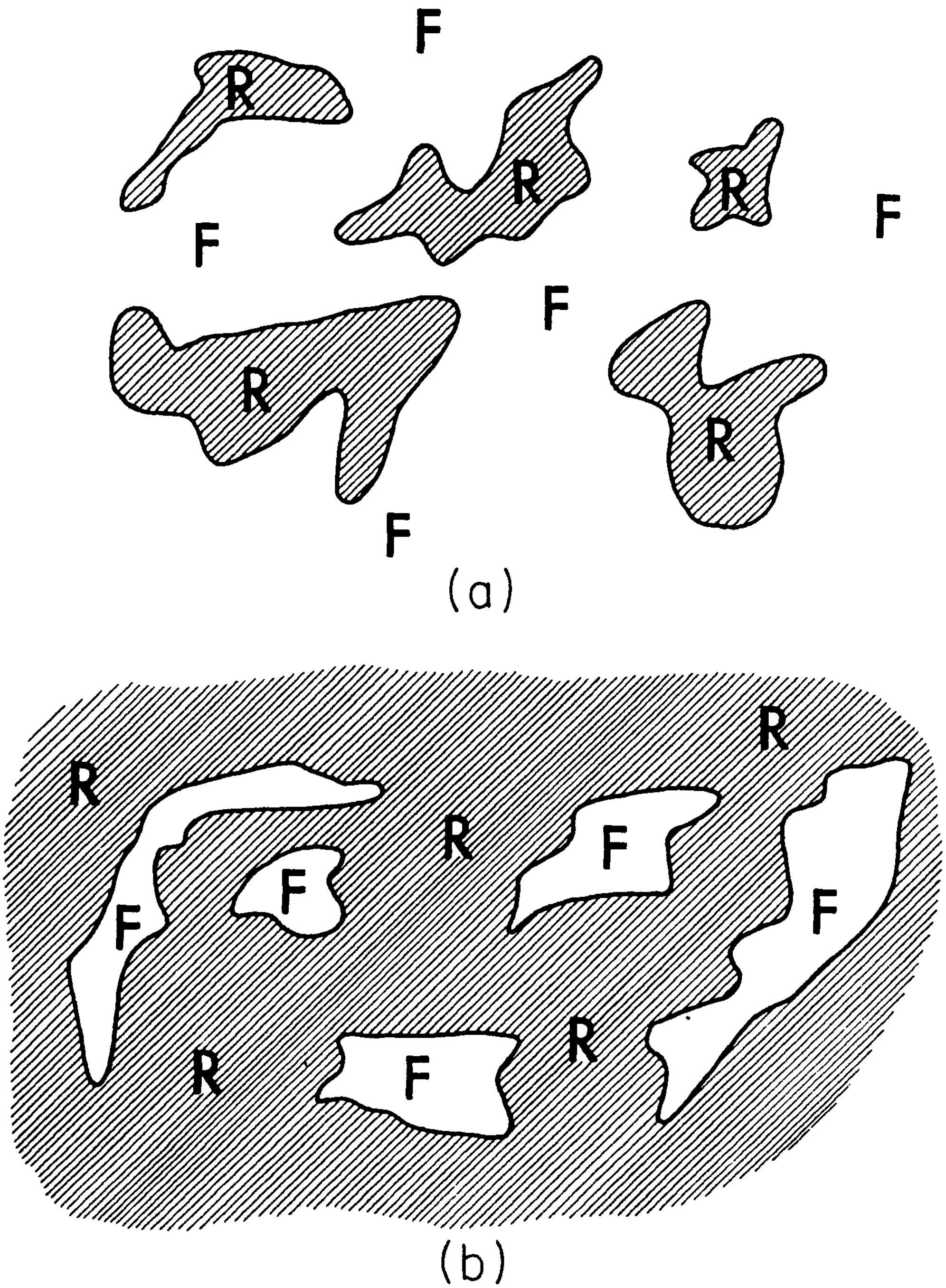


Figure 1 The transition from a floppy state, (a), to a rigid system, (b).

vector degrees of freedom per atom. For example, if there are only CFs between the atoms, one has $N_{\mathrm{con}} = N_d = Z/2$, where Z is the number of the nearest neighbor atoms. Phillips [18] also discussed the idea of *underconstrained* and *overconstrained* glasses. Underconstrained glasses are those that have a high coordination number, possess non-zero elastic moduli and, therefore, are in the form of amorphous solids. Overconstrained glasses, on the other hand, are those with a low coordination number, have no elastic moduli, are not mechanically stable, and are in the form of polymeric glasses. Consider, as an example, the Ge_xSe_{1-x} systems. If $x < 0.2$, then, the compound is a polymer chain of Se with some Ge crosslinks. However, if $x > 0.2$, then, one has a strong and mechanically stable network with non-zero elastic moduli. Phillips [18] proposed that if the average coordination number $\bar{Z}$ of the system is less than about 2.4, then, the system is essentially a polymeric glass, whereas if $\bar{Z} > 2.4$, then, one has an amorphous solid. Thorpe [19] discussed essentially the same ideas, albeit in a more formal way, and called the underconstrained and overconstrained regions *rigid* and *floppy*, respectively. Figure 1 shows the differences between the two systems.

From this description of the morphological phase transition in glassy networks and that of EPNs discussed in section 2, it may be clear that the underconstrained and overconstrained regions correspond, respectively, to an EPN *above* or *below* the percolation threshold. If so, then, one may use such networks to study not only elastic properties of glassy networks, as a function of its average coordination number $\bar{Z}$, but also any other property that may be of interest. We have carried out MC calculations using a BCC network ($Z = 8$) to study an EPN with CFs only, and a simple-cubic network ($Z = 6$) to investigate the BB model. We calculated the elastic constant C_{11} of the network as a function of the average coordination number $\bar{Z} = pZ$, which is varied by depleting at random a fraction $q = 1 - p$ of the springs, and calculating C_{11} by the numerical method described above, where Z is the coordination number of the intact ($p = 1$) network. The depleted springs correspond to floppy regions (since for such springs we set $e = 0$), whereas the intact or present springs represent the rigid or underconstrained regions. The results for the CF and BB models are presented in Figure 2, together with the results for the KK model in a diamond network for which $Z = 4$ [20]. It is clear that as $\bar{Z}$ decreases, the elastic constant C_{11} also decreases and eventually vanishes at some critical value of $\bar{Z}$, which depends on the microscopic force laws that the springs obey. Similar results are obtained if we calculate other elastic moduli of the networks, e.g., Young's or shear modulus. As Figure 2 indicates the qualitative aspects of all three models are similar. However, as can be seen in Figure 2, and in agreement with the theoretical discussion of section 2, a CF system requires the highest average coordination number in order to have a non-zero elastic modulus, whereas the BB system needs the smallest $\bar{Z}$ in order to become rigid and possess non-zero elastic moduli. In between lies the KK system which, although in two dimensions becomes rigid at the same $\bar{Z}$ as the BB model, it requires a higher coordination number than the BB model in three dimensions in order to support stress transport and have non-zero elastic moduli. Note that the main difference between the KK and BB models is that, in the former system the bending of colinear bonds was not allowed. The range of interaction of one site of the network with its neighbors in the BB model is also somewhat longer than that in the KK system. Therefore, microscopic (interatomic) force laws, and the range of interaction between the atoms play a fundamental role in determining the mechanical properties and stability of disordered materials.

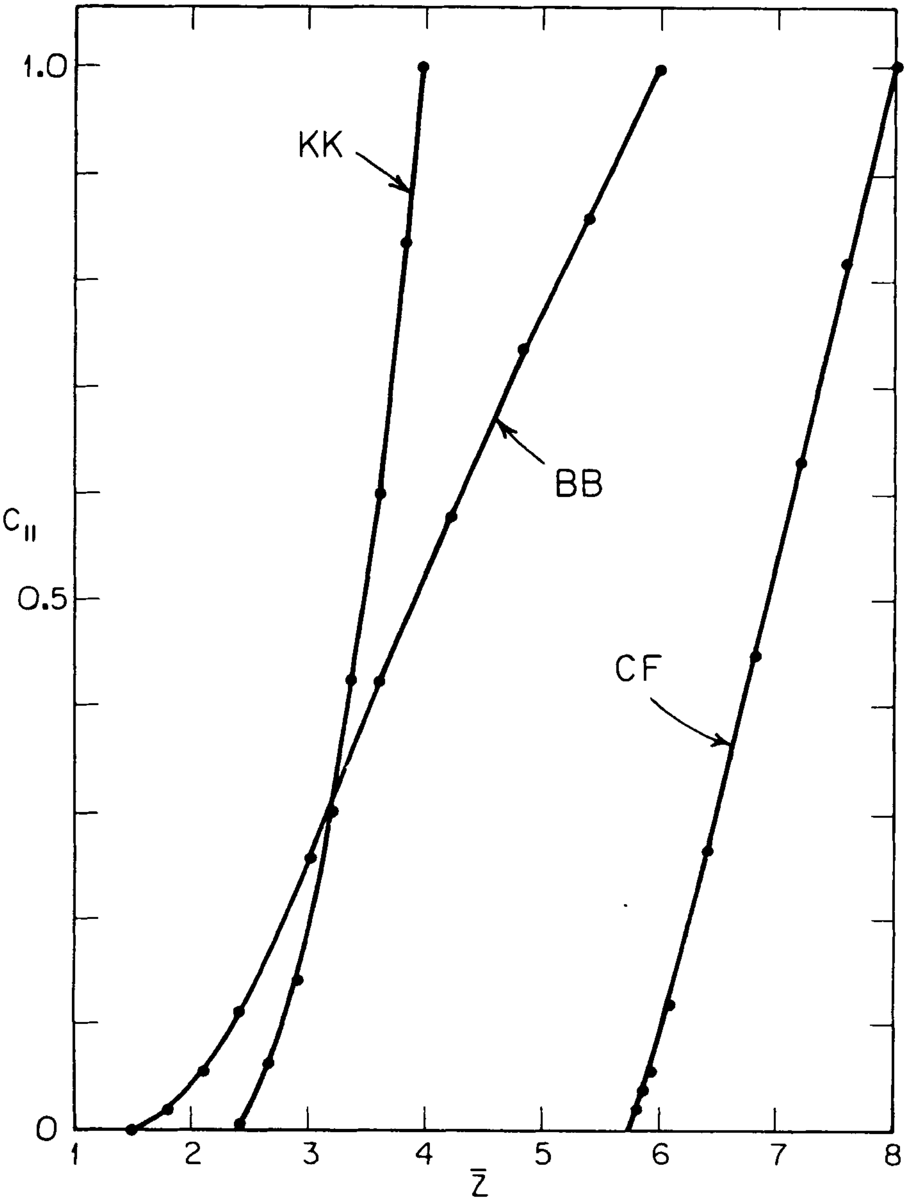


Figure 2 Variations of the elastic modulus C_{11} with the average coordination number $\bar{Z}$ of three-dimensional elastic percolation networks.

As Figure 2 shows, in the KK model the elastic constant C_{11} vanishes at about $\bar{Z} \simeq 2.4$, which is the same as that proposed by Phillips [18] for macroscopic rigidity of glassy networks. Thus, such networks have an unusual property: although for $1.5 < \bar{Z} < 2.4$ they are geometrically connected and a sample-spanning of interconnected atoms does exist [since at the connectivity or scalar percolation threshold,

$\bar{Z} \simeq 1.5$; see Equation (12)], they are *not* mechanically stable and do not have any non-zero elastic modulus. The reason is that there are many configurations of the sample-spanning cluster which can be deformed at no cost to the elastic energy of the system. In the BB model, on the other hand, any deformation of the system is done at a cost to the elastic energy of the system and, therefore, $p_e^B = p_c^B$. We should point out that, although the results of Figure 2 were obtained with three different networks, namely, the diamond, simple-cubic and BCC networks, these results are *independent* of the type of the network since, according to Equations (10)–(12), the average coordination number of the system at the percolation threshold is invariant with respect to the type of the network and depends only on d, the dimensionality of the network. Therefore, if for example, for the CF model calculations, we had used a face-centered cubic network ($Z = 12$) instead of a BCC network, we would still have observed that C_{11} vanishes at $\bar{Z} \simeq 2d = 2 \times 3 = 6$. Thus, EPNs may be used to study morphological and other properties of glassy networks. This is not only confirmed by the results of Figure 2, but also by the very recent experimental work of Love *et al.* [21] who studied ten different glass compositions in the Ge–As–Se system, and investigated their relaxation of persistent infrared spectral holes burned in the SeH vibrational absorption band. They found that a single parameter, the average coordination number $\bar{Z}$ of the system, can predict the spectral-hole relaxation, and that for all ten systems, $2 \leqslant \bar{Z} \leqslant 2.8$, with an average of about 2.4, in agreement with Phillips's idea [18] and the simulations based on EPNs reported here.

4 TRANSPORT, MECHANICAL AND RHEOLOGICAL PROPERTIES OF POLYMERS AND COMPOSITE SOLIDS

Another class of materials whose properties can be modeled and studied by the EPNs described here includes gel polymers, colloidal aggregates and composite solids. Experimental studies of scalar transport (e.g., conduction) and vector transport (elasticity) in such systems are nowadays being carried out more frequently than in the past, because of the advances in accurate measurements and the importance of the properties of such disordered materials. One is particularly interested in the properties of such materials near a phase transition point, e.g., the GP where a transition from a liquid-like system to an elastic solid takes place, since experimental data suggest that many properties of these materials obey universal scaling laws near the phase transition point which do not depend on the microscopic details of the system. These universal scaling laws are similar to those in thermal systems near the critical temperature. However, experimental determination of the macroscopic properties of such materials (conductivity, elastic moduli) is often difficult to be made right at, or near, the phase transition point of the system, if for no reason other than the fact that phase transition points are usually defined for *infinite* systems, whereas in most practical situations one deals with a *finite* system. Moreover, some of the measurements (especially those of rheological properties) are done when the system is in a transient state, whereas the apparent scaling laws are for static, or steady state, or zero frequency limits. Such difficulties have been a source, among others, to cause some disagreement between the experimental results and the predictions of various models, as discussed below.

Consider for example, a gelling solution below the GP, as a common example of a disordered system, which consists of a sol (liquid) that contains an assembly of polydisperse finite polymers or clusters. For $\phi > \phi_c$, where ϕ represents the fraction of the monomers (or the sites) in the polymers and ϕ_c its value at the GP, there is an infinite gel network. At ϕ_c, the gelling solution undergoes a transition from a liquid-like medium to an elastic solid which has unique and unusual properties: its elastic moduli G_e are zero whereas its viscosity η is infinite. One of our main goals is to study G_e and η near ϕ_c using EPNs.

Let us first discuss a few properties of EPNs which are relevant to our study here. It is generally believed, based on computer simulations, an exactly-solved model, and renormalization group theory of Feng and Sahimi [22], that in an EPN above and near the percolation threshold *all* elastic moduli G_p of the system obey a universal scaling law in the form

$$G_p \sim (p - p_c)^{f_p}, \tag{14}$$

where, depending on the model, p_c can be the scalar threshold (for the BB model) or the elastic threshold (for the CF model). The electrical or thermal conductivity σ_p of the same system (if the present or active bonds between sites are conducting) obeys

$$\sigma_p \sim (p - p_c)^t. \tag{15}$$

The *critical exponent t* is universal and independent of the microscopic details of the system. Similar to thermal systems near the critical temperature, one can also define a percolation correlation length ξ_p which obeys a universal scaling law near p_c

$$\xi_p \sim (p - p_c)^{-\nu_p}. \tag{16}$$

and an order parameter $P(p)$ which obeys

$$P(p) \sim (p - p_c)^{\beta_p}. \tag{17}$$

The physical significance of ξ_p is that, only for length scales $L > \xi_p$, the system is macroscopically homogeneous. For $L < \xi_p$ the sample-spanning percolation cluster is a self-similar fractal object, such that its total mass M (i.e., its total number of active bonds or sites) scales with L as $M \sim L^{d_f}$, where

$$d_f = d - \beta_p/\nu_p, \tag{18}$$

for a d-dimensional system. The physical meaning of $P(p)$ is that it is the *fraction* of active bonds or sites in the sample-spanning cluster. In Table 2 we show the currently-accepted values of the exponents. For the BB model, Sahimi [23] proposed a scaling relation between f_p, t and ν_p which is given by

$$f_p = t + 2\nu_p \tag{19}$$

which is supported by the existing numerical values of these exponents (see below).

On the other hand, many experimental sets of data for gel polymers and composite solids indicate similar behavior. In particular, experimental data on gel polymers indicate that near ϕ_c

$$G_e \sim (\phi - \phi_c)^{f_e}. \tag{20}$$

A similar scaling law was found for the elastic moduli of sintered, submicron, silver powder beams near their critical percolation-volume fraction [4]. For the viscosity of a gelling solution *below* and near ϕ_c, it has been found that

$$\eta \sim (\phi_c - \phi)^{-k}. \tag{21}$$

It is clear that there is a one-to-one correspondence between G_p and G_e and, therefore, one might hope that, $f_e = f_p$, and that accurate estimates of f_e can be obtained by estimating f_p using EPNs. On the other hand, at first sight, there seems to be no analog of η in a percolation network. However, if in an EPN a fraction p of the springs are perfectly rigid (with an infinite elastic constant) and the rest are soft (finite elastic constant), then, the elastic moduli G_p of this system, the SEPN discussed in section 2, diverse as

$$G_p \sim (p_c - p)^{-\tau}, \tag{22}$$

which might indicate that there is an analogy between G_p, given by Equation (22), and η. We show that this is indeed the case. But let us first briefly discuss the available experimental data, before presenting our results. We first discuss the gel polymer systems near the GP.

Experimental investigations of sol-gel transitions usually proceed by measuring the time evolution of the relevant quantities (e.g., viscosity) during the chemical reaction leading to gelation, assuming that the experimental parameter (time or frequency) and the theoretical one (the number of crosslinks) are linearly related in the vicinity of the transition (gelation) point. This assumption is not obvious and has been criticised by some researchers. Rheological measurements are usually performed by using a conventional cone and plate rheometer or by a more accurate magnetic sphere rheometer. The ranges of shear rates and deformations and times of measurements of these devices allow the determination of the steady-state zero-shear viscosity and the steady-state linear elastic modulus up to the *vicinity* of the phase transition or the GP, which is a percolation threshold, but it has proven to be more difficult to do such measurements at the GP.

Experimental determination of k encounters many difficulties. The major obstacles are that one can not accurately pinpoint the transition point in the experiments and, moreover, the measurements can not be made *right* at the GP and in the *limit of zero frequency*. In obtaining k, the real and imaginary parts of the frequency-dependent complex modulus,

$$\bar{G}(\omega) = G'(\omega) + iG''(\omega), \tag{23}$$

are usually measured, where G' (storage modulus) and G'' (loss modulus) describe, respectively, storage and dissipation in an oscillating strain field of constant amplitude. These components of the complex shear modulus $\bar{G}(\omega)$ are predicted to scale with frequency as

$$G' \sim G'' \sim \omega^{\Delta} \tag{24}$$

at the GP. During the formation of the gel network in the reaction bath, there are usually two limiting states. The first case is the so-called Zimm limit [24, 25] in which there are strong hydrodynamic interactions between monomers and also the polymers of various sizes. In this limit, polymeric cluster relaxation is governed by Stokes–Einstein relation. The surroundings of any molecule is composed of smaller clusters which are stationary on the molecular time scale. Because of this, one may hope that a static percolation network can be used to model the divergence of η. That this can indeed be done is shown later in this paper. In the opposite second case, the Rouse limit [25], there are no hydrodynamic interactions between the various polymers in the reaction both with relaxation times proportional to their masses. Under these conditions, the so-called viscoelastic exponent Δ is related [26] to the zero frequency exponents f_e and k by

$$\Delta = \frac{f_e}{k + f_e}. \tag{25}$$

The fact that these moduli *cannot* be measured right at the GP makes them frequency-dependent. This not only introduces more variations in the data, but also makes their comparison with the percolation predictions more difficult. On the other hand, percolation thresholds of any network can be determined either exactly or accurately by numerical simulations. Furthermore, elastic moduli *can* be determined right at the percolation threshold and in the limit of zero frequency.

In general, most recent experimental data indicate that G_e vanish with an exponent in the range of 3.2–3.8. However, a few older experiments have given an exponent close to 2. Experimental data on η indicate that it diverges with an exponent k the value of which is either mostly in the range 0.6–0.8, or is in the range 1.3–1.5. Some of the more notable experimental investigations are as follows.

In 1979, Adam *et al.* [27] reported on viscosity measurements taken during the copolymerization of Styrene Divinylbenzene in the reaction bath near the GP. Their result, obtained by using a magnetic sphere rheometer was, $k = 0.78 \pm 0.1$. Another set of rheological measurements on hydrolyzed polyacrylamide yielded $k = 0.9 \pm 0.2$ [28]. As mentioned earlier, there exist some experimental results for k in the range of 1.3–1.5. For example, Martin *et al.* [29] directly measured the divergence of the viscosity of epoxy resins and found that $k = 1.4 \pm 0.2$, which, as we shall show, must be in the Rouse regime. Somewhat similar value of $k = 1.1 \pm 0.1$ was found from the viscosity measurements of a commercial hydrolysed polyacrylamide [28].

Many researchers have determined the viscoelastic exponent Δ, instead of finding k directly. Durand and co-workers [26] performed rheological measurements in a conventional cone-and-plate rheometer. A sinusoidal strain wave was applied and the resulting stress was analyzed in order to determine the moduli G' and G''. They obtained a mean value of $\Delta = 0.69 \pm 0.04$ near the GP. Martin *et al.* [29] also found $\Delta = 0.70 \pm 0.05$ at the GP. Similar results were obtained for a polyester system [30] with $\Delta = 0.69 \pm 0.02$. Very recently, Hodgson and Amis [31] used an extremely sensitive viscoelastic instrument, a multiple lumped resonator instrument, to study G' and G'' at very low frequencies (as low as 104 Hz). They also found that $\Delta \sim 0.70$ for a tetraethylorthosilicate reaction at the GP.

In the case of the elastic moduli, we can also classify the experimental data on f_e into two sets. Earlier measurements have resulted in values of f_e close to 2. Examples include the work in Reference [28], in which it was found that $f_e = 1.9 \pm 0.1$. In this work, elasticity of hydrolysed polyacrylamide near the GP was measured. To interpret the results in terms of the above scaling laws, the assumption was made that there exists a linear variation between t and ϕ, the monomers or the crosslinks fraction, in the critical region. The linear variation of ϕ with t is in fact a non-critical behavior of the reaction rate. Furthermore, the authors [28] mention that determination of both f_e and k is strongly dependent on the choice of the gelation time. Similar results for f_e were also found in the measurements by Zosel [32] and by Allain and Salomé [33].

The other larger set of experiments gives values for f_e, for both gel polymers and other disordered solids, in the range of 3.6–3.9. Deptuck, Harrison and Zawadzki [4] made measurements of the Young's modulus of a set of sintered, submicron, silver-powder beams near their critical percolation-volume fraction, and found

Table 2 Currently-accepted values of the critical exponents in d dimensions.

d	ν_p	β_p	d_f	t	s
2	4/3	5/36	91/48	1.2993 ± 0.0015	1.2993 ± 0.0015
3	0.88	0.41	2.534	2.003 ± 0.047	0.735 ± 0.005

$f_e = 3.8 \pm 0.5$. Furthermore, for the electrical conductivity of the system, they found that $t \simeq 2.15 \pm 0.2$, which is entirely consistent with percolation prediction (see Table 2). Woignier, Phalippou, Sempere, and Pelons [34] measured the Young's modulus of silica aerogels using the three points flexural technique, and found $f_e = 3.9 \pm 0.2$. Gauthier-Manuel, Guyon, Roux, Gits and Lefaucheux [35] measured the elasticity of silica particles during gelation in NaCl solutions and in pure water, and obtained $f_e = 3.8 \pm 0.2$. However, it is interesting to note that some of these gels are the so-called *physical gels* in which no chemical reaction takes place to form the gel network. On the other hand, even for the *chemical gels* an exponent f_e in the range of 3.2–3.8 has been found, e.g., the measurements of Adam *et al.* [36] who obtained $f_e \simeq 3.2 \pm 0.6$ for polycondensation.

We now show that the EPNs described above can explain the above mentioned experimental data. To begin with, we mention two major controversies regarding the scaling behavior of G_e and η near the GP. de Gennes [37] proposed that the elastic moduli of gel polymers near ϕ_c and the *conductivity* of percolation networks near p_c belong to the same universality class. That is, the critical exponents characterizing them near the GP or the percolation threshold are equal, $f_e = t$. He also proposed [38] that the divergence of the viscosity η of gel polymers near the GP point is similar to the divergence of the conductivity of a *superconducting* percolation network (SCPN) near p_c. In a SCPN, which is the scalar analog of a SEPN, a fraction p of bonds are perfect conductors (their resistance is zero), and the rest have a finite conductance (resistance). For such a network, one has

$$\sigma_p \sim (p_c - p)^{-s} \tag{26}$$

near p_c. Currently-accepted values of s are also listed in Table 2. These two conjectures of de Gennes have been quite controversial, since most of the experimental data have not been accurate enough to decisively favor or disfavor them. However, as far as the analogy between η and σ_p in a SCPN is concerned, we contend that [39] the behavior of σ_p in a SCPN has no relation with η near the GP because, in general, the rotation and deformation of finite polymers in local shears should make k smaller than s. Such deformations and rotational motions also make the field equations for σ_p totally different from those for η. Indeed, η is related to a tensor quantity [complex shear modulus; see Equation (22)], whereas σ_p is a scalar quantity and, therefore, there is no reason to believe that the scaling of η may be related to that of σ_p.

We now estimate the critical exponents of EPNs and SEPNs and relate them to those of G_e and η. The standard technique for estimating such critical exponents is the finite-size scaling method (FSSM) [40]. If we combine Equations (14) and (16), we obtain

$$G_p \sim \xi_p^{-\delta} \tag{27}$$

where $\delta = f_p/\nu_p$. In principle, Equations (14)–(17) are valid for infinitely large systems, whereas in practice one deals with a finite system. In such a system, the correlation length ξ_p of the system cannot exceed L, so that if $\xi_p > L$ we should write

$$G_p \sim L^{-\delta}. \tag{28}$$

Equation (28) is the essence of FSSM, which is written in analogy with FSSM for thermal systems near their critical temperature [41]. More generally, Equation (28) is written as

$$G_p \sim L^{-\delta} f(x) \tag{29}$$

where $x \propto (L/\xi_p)^{1/\nu_p}$. Equation (29) is valid for very large values of L (but such that $L < \xi_p$). In practice, one cannot use very large networks, so that correction-to-scaling terms become important. In such a case equation (29) is rewritten as

$$G_p \sim L^{-\delta}[1 + a_1 g_1(L) + a_2 g_2(L)]. \tag{30}$$

Here $g_1(L)$ and $g_2(L)$ represent, respectively, the leading non-analytical and analytical corrections to scaling, which are particularly important for small to moderate values of L, and a_1 and a_2 are constant. In a similar way, for a SEPN, we can write

$$G_p \sim L^{x}[1 + b_1 h_1(L) + b_2 h_2(L)], \tag{31}$$

where $x = \tau/\nu_p$. We recently showed that [42], $h_1(L) = g_1(L)$ and $h_2(L) = g_2(L)$, and that [42], for *all* transport properties of percolation networks (e.g., conductivity, elastic moduli, diffusivity, etc.), one has

$$g_1(L) = (\ln L)^{-1}, \tag{32}$$

$$g_2(L) = L^{-1}. \tag{33}$$

Since Equations (29) and (30) are supposed to be valid in a regime where $\xi_p > L$, the calculations are usually done at $p = p_c$, where ξ_p is divergent and is larger than any L that can be used in the simulations

We first used the BB model in a simple-cubic network, and carry out large scale MC calculations at $p_e^B = p_c^B \simeq 0.249$, using various values of L. The results are shown in Figure 3, where we present the variations of the Young's modulus K with L. In general, the scaling behavior of elastic moduli are independent of β/α, the ratio of BB and stretching force constants and, therefore, we used a small value, $\beta/\alpha = 0.04$, since smaller values of β/α accelerate the convergence of the solution for the linear set of equations for the nodal displacements (discussed in section 2) and the resulting elastic moduli to their true asymptotic behavior expressed by Equation (28). A fit of the results to Equations (30), (32) and (33) yields $\delta = f_p/\nu_p \simeq 4.3 \pm 0.1$, which, together with the currently-accepted value of ν_p (Table 1), $\nu_p \simeq 0.88$, yield

$$f_p \simeq 3.78 \pm 0.09. \tag{34}$$

This is consistent with those experimental data for G_e which are mostly in the range 3.2–3.8. As discussed above, one source of some discrepancy between the data and the percolation prediction is the fact that the experimental measurements are carried out at a finite frequency ω, whereas the percolation predictions are strictly valid for the limit $\omega = 0$. Finite frequencies usually result in values of the critical exponents that are lower than their asymptotic (zero frequency) values.

We now turn our attention to those experimental data for G_e which indicate that, $f_e \simeq 2$. To explain this set of experimental data, we used the Born model described above, and carried out FSS calculations at $p_c^B \simeq 0.249$ in a simple-cubic network. We

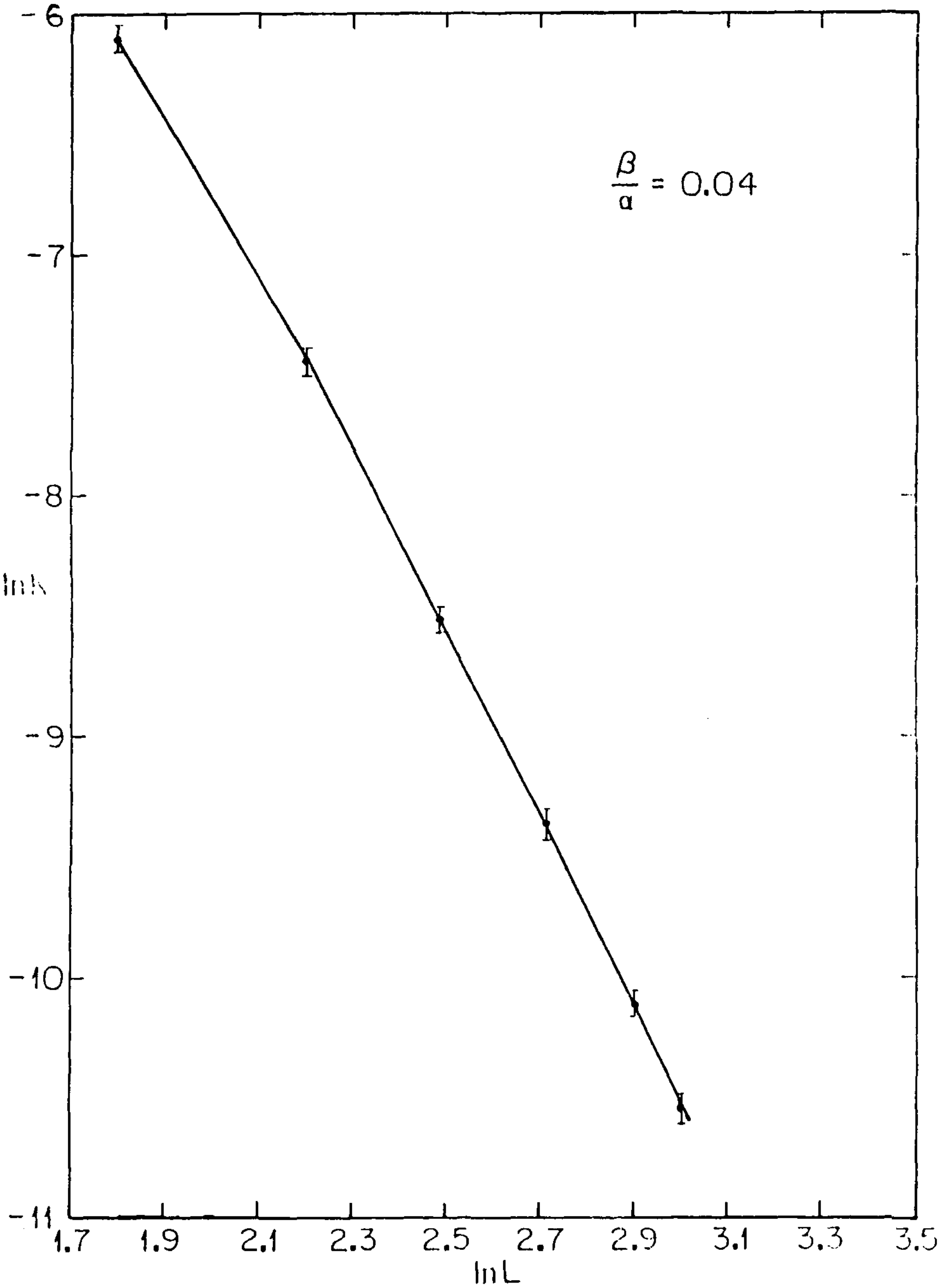


Figure 3 Variations of the Young's modulus K with the linear size L of the elastic network, in the BB model at the bond percolation threshold of the cubic network.

obtained, $f_p \simeq 2.03 \pm 0.06$, which is totally consistent with the data. Calculations with the CF model yielded a similar result. We can now understand why there are two distinct sets of experimental data, each pointing to a distinct value of f_e. If in a polymer network near its critical point the BB contributions to the elastic energy of the system dominate all other sources of contributions, then, the elastic moduli of the system obey a power law scaling near the critical point whose exponent is given by that of the BB or KK model [see Equations (3)–(6)], $f_e = f_p \simeq 3.8$. If, on the other hand, the largest contribution to the elastic energy of the system comes from scalar-like terms [for example, the second term of Equation (2)], or if only CF contributions are present, then, the critical exponent of the elastic moduli is given by $f_e \simeq t \simeq 2$.

How can we explain the experimental data on the scaling behavior of η near the GP? To begin with, we propose that the behavior of η near the GP is analogous to that of the shear modulus κ of a SEPN near p_c. However, this is not nearly enough to explain the scaling of η near the GP since, as discussed above, experimental data indicate that the value of k is either in the range 0.6–0.8, or in the range 1.3–1.5, whereas a SEPN is characterized by a unique critical exponent τ. The reason for the existence of two distinct values of k is the fact that below the GP, the system can be in the Zimm or Rouse limits whose dynamics are totally different, and this may explain why one obtains two distinct values of k. Note that above the GP the Zimm or Rouse dynamics can not affect the value of f_e, since above the GP the system is completely dominated by a very large (and static) polymer network and, therefore, the absence or presence of diffusion of small polymers (as in the Zimm or Rouse limits), which are not attached to the main polymer network, cannot affect the value of f_e. This is why the reason for the two distinct values of k is different from that for the two distinct values of f_e discussed above.

Based on the proposed analogy between κ and η, we use a SEPN and attempt to simulate the Zimm limit and Rouse limits. As discussed above, in the Zimm limit near ϕ_c, there is little or no polymer diffusion because of the strong hydrodynamic interactions. Hence, a SEPN, which is a static system, may suffice for simulating the Zimm limit. Therefore, we used the BB model in a simple-cubic network, carried out large scale MC calculations at $p_e^B = p_c^B \simeq 0.249$, and used Equations (31)–(33) to estimate $x = \tau/\nu_p$. The results are shown in Figure 4, from which we obtain $x \simeq 0.74 \pm 0.04$, which means that

$$\tau \simeq 0.65 \pm 0.03. \tag{35}$$

This value of τ is consistent with those experimental data for k which are mostly in the range 0.6–0.8, which also indicates that such measurements were presumably done in the Zimm limit (i.e., no significant diffusion of the polymers).

On the other hand, there are no hydrodynamic interactions between the polymers in the Rouse limit and, therefore, polymers of various sizes can diffuse essentially freely in the reaction bath. Therefore, to simulate this regime we first generate a SEPN. Each cluster of totally rigid springs represents a polymer of given size, and there is a wide distribution of such polymers in the network. The soft springs represent the liquid medium in which the rigid clusters or polymers diffuse. At each time step, a randomly-selected fraction of rigid clusters are moved, with equal probability, in one principal direction of the network. This simulates the diffusion of the polymers in the reaction bath and, as such, this SEPN is a *dynamic* system. 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 then calculate κ, move another randomly-selected

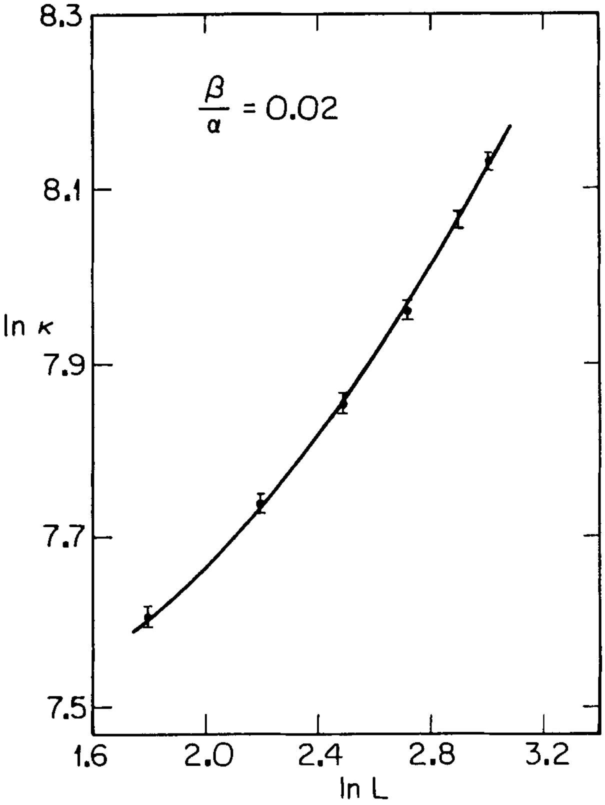


Figure 4 Variations of the shear modulus κ of the superelastic percolation network with the linear size L of the system, in the BB model at the bond percolation threshold of the cubic network.

fraction of rigid clusters, determine κ again and so on. Computations are carried out for enough steps until κ achieves an essentially constant value. Using this method, together with the BB model in a simple-cubic network and FSSM, we obtain

$$\tau \simeq 1.4 \pm 0.1. \qquad (36)$$

This is consistent with those experimental data for k which are in the range 1.3–1.5, which also indicates that these measurements were presumably done in the Rouse limits (i.e., with strong polymer diffusion).

Our results indicate that the dynamics of polymer diffusion in the reaction bath plays a fundamental role in the scaling behavior of the *viscosity* of the gelling solution near and *below* the GP, but may play no role in the scaling behavior of *elasticity* gel polymers *above* and near the GP. On the other hand, the contribution of various forms of deformation of the polymer network to its elastic energy plays a fundamental role in the scaling behavior of the elasticity of the polymer near the critical point, whereas it does not play a significant role in the scaling behavior of η near the GP, since when measuring η, the system is still liquid-like and, therefore, deformations can play no important role. Finally, it is worth mentioning that we have succeeded in relating τ to the critical exponents ν_p and β_p defined above. We have proposed that [39]

$$\tau = \nu_p - \beta_p/2, \quad \text{Zimm limit} \tag{37}$$

$$\tau = 2\nu_p - \beta_p, \quad \text{Rouse limit} \tag{38}$$

which are in complete agreement with out estimate of τ for the two regimes and the numerical estimates of ν_p and β_p (Table 1), and also consistent with our interpretation of the data.

5 SUMMARY AND CONCLUSIONS

We have developed elastic and superelastic percolation models to explain the experimental data on morphological, mechanical and rheological properties of a large class of materials, including polymers, composite solids, colloidal aggregates and glassy networks. Our models clearly demonstrate the fundamental role that the connectivity and microscopic laws of stress transport play in determining various properties of such materials. Moreover, our models reveal the existence of universal scaling laws for mechanical and rheological properties of such materials, and provide a consistent explanation for the experimental data.

In this paper, we only considered linear and static (zero frequency) properties of disordered materials. However, our models can be generalized for studying their non-linear and dynamic properties as well. For example, they can be used to study the formation and propagation of cracks in disordered materials, which are of immense scientific and industrial importance. Work along these lines is reported elsewhere [43–45].

Acknowledgements

This work was supported in part by the National Science Foundation Grant No. CST 8615160, the U.S. Air Force Office of Scientific Research Grant No. 87-0284, and the San Diego Supercomputer Center.

References

[1] K.K. Mohanty, Ph.D. Thesis, University of Minnesota, Minneapolis (1981).

[2] D. Stauffer, *Introduction to Percolation Theory*, Taylor and Francis, London (1985).

[3] D. Stauffer, "Gelation in Concentrated Critically Branched Polymer Solutions," *J. Chem. Soc. Faraday Trans. II*, **72**, 1354 (1976).

[4] D. Deptuck, J.P. Harrison and P. Zawadzki, "Measurements of Elasticity and Conductivity of a Three-Dimensional Percolation System," *Phys. Rev. Lett.*, **54**, 913 (1985).

[5] S. Mall and W.B. Russel, "Effectice Medium Approximation for an Elastic Network Model of Flocculated Suspensions," *J. Rheol.*, **31**, 651 (1987).

[6] M. Sahimi, G.R. Gavalas and T.T. Tsotsis, "Statistical and Continuum Models of Fluid-Solid Reactions in Porous Media," *Chem. Eng. Sci.*, **45**, 1443 (1990).

[7] M.H. Cohen and G.S. Grest, "Liquid-Glass Transition, a Free-Volume Approach," *Phys. Rev.*, **B20**, 1077 (1979).

[8] S. Feng and P.N. Sen, "Percolation on Elastic Networks: New Exponent and Threshold," *Phys. Rev. Lett.*, **52**, 216 (1984).

[9] G.R. Jerauld, Ph.D. Thesis, University of Minnesota, Minneapolis (1985).

[10] A. Hansen and S. Roux, "Universality Class of Central-Force Percolation," *Phys. Rev.*, **B40**, 749 (1989).

[11] M. Sahimi and S. Arbabi, "Force Distribution, Multiscaling and Fluctuations in Disordered Elastic Media," *Phys. Rev.*, **B40**, 4975 (1989).

[12] S. Arbabi and M. Sahimi, *Phys. Rev. B*, to be published (1991).

[13] J.G. Kirkwood, "The Skeletal Modes of Vibration of Long Chain Molecules," *J. Chem. Phys.*, **7**, 506 (1939).

[14] P.N. Keating, "Relationship Between the Macroscopic and Microscopic Theory of Crystal Elasticity. I. Primitive Crystals," *Phys. Rev.*, **152**, 774 (1966).

[15] J.C. Phillips and M.F. Thorpe, "Constraint Theory, Vector Percolation and Glass Formation," *Solid State Commun.*, **53**, 699 (1985).

[16] V.K.S. Shante and S. Kirkpatrick, "An Introduction to Percolation Theory," *Adv. Phys.*, **20**, 325 (1971).

[17] S. Feng, M.F. Thorpe and E.J. Garboczi, "Effective-Medium Theory of Percolation on Central-Force Elastic Networks," *Phys. Rev.*, **B31**, 276 (1985).

[18] J.C. Phillips, "Topology of Covalent Non-Crystalline Solids. I: Short-Range Order in Chalcogenide Alloys," *J. Non-Crystalline Solids*, **34**, 153 (1979).

[19] M.F. Thorpe, "Continuous Deformation in Random Networks," *J. Non-Crystalline Solids*, **57**, 355 (1983).

[20] H. He and M.F. Thorpe, "Elastic Properties of Glasses," *Phys. Rev. Lett.*, **54**, 2107 (1985).

[21] S.P. Love, A.J. Sievers, B.L. Halfpap and S.M. Lindsay, "Effects of Network Topology on Low-Temperature Relaxation in Ge-As-Se Glasses, as Probed by Persistent Infrared Spectral Hole Burning," *Phys. Rev. Lett.*, **65**, 1792 (1990).

[22] S. Feng and M. Sahimi, "Position-Space Renormalization for Elastic Percolation Networks with Bond-Bending Forces," *Phys. Rev.*, **B31**, 1671 (1985).

[23] M. Sahimi, "Relation Between the Critical Exponent of Elastic Percolation Networks and the Dynamical and Geometrical Exponents," *J. Phys. C*, **19**, L79 (1986).

[24] P.G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, New York (1979).

[25] W.H. Stockmayer, *Molecular Fluids*, Gordon and Breach, New York (1976).

[26] D. Durand, M. Delsanti, M. Adam and J.M. Luck, "Frequency Dependence of Viscoelastic Properties of Branched Polymers Near Gelation Threshold," *Europhys. Lett.*, **3**, 297 (1987).

[27] M. Adam, M. Delsanti, R. Okesha and G. Hild, "Viscosity Study in the Reaction Bath of the Radical Copolymerization of Styrene Divinylbenzene," *J. Physique Lett.*, **40**, L359 (1979).

[28] C. Allain and L. Salomé, "Hydrolysed Polyacrylamide/Cr^{3+} Gelation: Critical Behavior of the Rheological Properties at the Sol-Gel Transition," *Polymer Commun.*, **28**, 109 (1987).

[29] J.E. Martin, D. Adolf and J.P. Wilcoxon, "Viscoelasticity of Near-Critical Gels," *Phys. Rev. Lett.*, **61**, 2620 (1988).

[30] M. Rubinstein, R.H. Colby and J.R. Gillmore, *Polym. Prepr. Am. Chem., Soc. Div. Polym. Chem.* **30 (No. 1)**, 81 (1989).

[31] D.F. Hodgson and E.J. Amis, "Dynamic Viscoelastic Characterization of Sol-Gel Reactions,"*Macromolecules*, **23**, 2512 (1990).

[32] A. Zosel, "Rheological Properties of Disperse Systems at Low Shear Stresses," *Rheol. Acta.*, **21**, 72 (1982).

[33] C. Allain and L. Salomé, "Sol-Gel Transition of Hydrolyzed Polyacrylamide + Chromium III: Rheological Behavior versus Cross-link Concentration," *Macromolecules*, **20**, 2957 (1989).

[34] T. Woignier, J. Phalippou, R. Sempere and J. Pelons,"Analysis of the Elastic Behavior of Silica Aerogels taken as a Percolating System," *J. Phys. France*, **49**, 89 (1988).

[35] B. Gauthier-Manual, E. Guyon, S. Roux, S. Gits and F. Lefaucheux, "Critical Viscoelastic Study of the Gelation of Silica Particles," *J. Physique*, **48**, 869 (1988).

[36] M. Adam, M. Delsanti and D. Durand, "Mechanical Measurements in the Reaction Bath During the Polycondensation Reaction, Near the Gelation Threshold," *Macromolecules*, **18**, 2285 (1985).

[37] P.G. de Gennes, "On a Relation Between Percolation Theory and the Elasticity of Gels," *J. Physique Lett.*, **378**, L1 (1976).

[38] P.G. de Gennes, "Incoherent Scattering Near a Sol-Gel Transition," *J. Physique Lett.*, **40**, L197 (1979).

[39] S. Arbabi and M. Sahimi, "Critical Properties of Viscoelasticity of Gels and Elastic Percolation Networks," *Phys. Rev. Lett.*, **65**, 725 (1990).

[40] M. Sahimi, B.D. Hughes, L.E. Scriven and H.T. Davis, "Critical Exponent of Percolation Conductivity by Finite-Size Scaling," *J. Phys. C*, **16**, L521 (1983).

[41] M.E. Fisher, in *Critical Phenomena: Enrico Fermi Summer School*, Verenna, Italy, Course 51, M.S. Green (ed.), Academic Press, New York (1971), p. 1.

[42] M. Sahimi and S. Arbabi, "On Correction to Scaling for Two- and Three-Dimensional Scalar and Vector Percolation," *J. Stat. Phys.*, **62,** 453 (1991).

[43] M. Sahimi and J. D. Goddard, "Elastic Percolation Models for Cohesive Mechanical Failure in Heterogeneous Systems," *Phys. Rev.*, **B33,** 7848 (1986).

[44] S. Arbabi and M. Sahimi, "Test of Universality for Three-dimensional Models of Mechanical Breakdown in Disordered Media," *Phys. Rev.*, **B41,** 772 (1990).

[45] M. Sahimi and S. Arbabi, "Fixed Points and Universality Classes of Fracture of Disordered Solids and Granular Media," *J. Stat. Phys.* to be published (1991).