RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 3 1 FEBRUARY 1985

Dynamical behavior of fractal structures

Itzhak Webman and Gary S. Grest
Corporate Research Science Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801
(Received 3 December 1984)

We present a scaling theory for the vibrational properties of tenuous fractal objects and a numerical calculation of the density of states for percolation clusters and diffusion-limited aggregates. A microscopic elastic Hamiltonian is used, which contains bending energy terms and properly describes the elasticity of such structures. We find that the density of states is weakly divergent at low frequencies implying that fractal aggregates relax to a new configuration beyond a critical size.

Many physical systems have been made which have a fractal structure.[1,2] The vibrational properties and mechanical behavior of these systems are very different from those of ordinary compact objects. Here we present new predictions for the dynamical behavior and mechanical stability of such structures. Two examples of physical systems for which this discussion is of interest are as follows. (a) Random composite materials made out of rigid particles in a soft matrix such as polymer carbon-black composites. In this case the rigid component forms very large fractal clusters often near the percolation threshold.[3] (b) Colloidal aggregates such as gold and silica aggregates which are fractal over a wide range of lengths.[4-6] These structures are made up of units that are considerably larger than atomic size and remain stable in the configurations in which they are prepared. Other materials to which this theory could be relevant are microscopically disordered network materials such as gels and glasses.

Most disordered fractal structures are characterized by a preponderance of long wispy chainlike structural elements. Kantor and Webman[7] have suggested that the elasticity of such fractal structures is related to the elastic properties of thin rods and thin rigid plates. They show that the scaling of the elastic moduli of a fractal cluster differs markedly from that of the electrical conductivity or the dielectric constant. In this work we present a scaling theory which relates the static elastic behavior to the vibrational properties of such clusters. We then calculate the density of vibrational states. From our numerical results for the density of states at low frequencies we extract the values of the static scaling exponents, and compare it to the analytical values. We also present a calculation of the density of states obtained by the Born model which has been used to describe the vibrational properties of fractal systems[8-10] and show that the two models give very different results. The meaning of this difference and conditions for the correct choice of model are then discussed. The two systems studied are percolation fractals[11] and diffusion-limited aggregates (DLA).[12]

In the lattice model for fractal structures, a cluster is generated on a lattice which has a stochastic geometry analogous to that of the corresponding physical structure. For percolation clusters the lattice sites are randomly chosen with probability p. For $p \geq p_c$, a cluster which spans the sample can be separated from isolated clusters. This cluster is fractal up to a size scale ξ which diverges at p_c. Fractal aggregates can be created by diffusion-limited aggregation or by alternative stochastic growth methods.[13] The macroscopic rigidity of the material is determined by the elasticity of long, tortuous thin channels of rigid material which are contained in the cluster backbone. The elastic behavior of a tortuous thin rigid chain depends on the chain configuration.[7] The elasticity of a corresponding lattice chain within the scalar Born model depends only on the length of the chain, suggesting that this model may not be adequate. The model presented here leads to a correct representation of such continuous chains and can be expected to properly describe a continuous percolating system in the critical region, as well as more general fractal structures in which the elastic behavior is dominated by a stringy, tortuous backbone.

The elastic lattice Hamiltonian in two dimensions[14] has the form

$$H=\sum_i \left[G \sum_{\substack{j,k \\ (j,k \text{ NN of } i)}}^{c} \delta\phi_{jik}^2 + \frac{Q}{a^2} \sum_{\substack{j \\ (\text{NN})}}^{c} (\mathbf{u}_i-\mathbf{u}_j)_{\parallel}^2 \right] , \tag{1a}$$

where $(\mathbf{u}_i-\mathbf{u}_j)_{\parallel}$ is the relative displacement of the site j in the direction parallel to the bond (i,j), and $\delta\phi_{jik}$ is the change in the angle between the bonds (i,j) and (i,k) connected to site i. The summation $\sum^c$ is over nearest-neighbor lattice sites of i which belong to the cluster. G and Q are local elastic constants and a is the lattice constant. A second model which has been recently used to describe the vibrational properties of disordered fractals is the Born Hamiltonian[8-10]

$$H=\frac{1}{a^2} \sum_{\substack{i,j \\ (\text{NN})}}^{c} (\mathbf{u}_i-\mathbf{u}_j)^2 . \tag{1b}$$

Applying the elastic Hamiltonian of Eq. (1a) to a tortuous chain of N elastic bonds, it is found that the elastic energy E and the displacement of the end to end vector $\delta\mathbf{R}$ (Ref. 7) are related by

$$E=\tfrac{1}{2}\delta\mathbf{R}\hat{\mathbf{K}}\delta\mathbf{R} , \qquad \hat{\mathbf{K}}=\frac{G\hat{\mathbf{Z}}\hat{\mathbf{S}}^{-1}}{N} . \tag{2}$$

Here $\hat{\mathbf{S}}$ is the tensor of gyration of the chain, $\hat{\mathbf{Z}}$ represents a 90° rotation operator, and $\hat{\mathbf{K}}$ is an elastic tensor. In contrast, $\hat{\mathbf{K}} \propto \hat{\mathbf{I}}/N$ for Born model and the elastic properties do not depend on the chain configuration.

Generally, the elastic constants of a region of size L of the fractal depends on the structure of the backbone in that region. The backbone consists of both singly connected and

multiply connected bonds.[7,15] Assuming that the softness of a region is determined by the singly connected bonds gives

$$K(L) \sim \frac{1}{N_s(L) L^2} , \tag{3}$$

where $N_s(L)$ is the number of singly connected bonds in a region of size L. This is also an exact upper bound for K.[7]

The low-frequency vibrational modes of a fractal object in a finite region are determined by the structure of both the backbone and the dangling ends in the region. The backbone determines the elastic constant while the mass distribution is determined by both. Consider a region of size L of fractal structure of Hausdorff dimension D. A dilation of the length by a factor λ gives $K(\lambda L) = \lambda^{-\tilde{\zeta}_E} K(L)$, where $\tilde{\zeta}_E$ depends on certain geometrical features of the backbone of the specific fractal structure. The mass in a region of size L scales with L as $M(\lambda L) = \lambda^D M(L)$. From these relations we obtain the scaling property for the vibrational frequencies

$$\omega(\lambda L) = \lambda^{-(\tilde{\zeta}_E + D)/2} \omega(L) . \tag{4}$$

The density of vibrational states is approximately given by $\rho(\omega, L) \sim 1/L^D \Delta\omega$, where $\Delta\omega$ is the spacing between the frequencies of the low vibrational eigenmodes of a structure of size L. The spacing $\Delta\omega$ is of the order of the frequency of the lowest eigenstate, and it scales in the same manner as $\omega(L)$ in Eq. (4). These scaling relations can be combined to yield the exponent $\tilde{d}_E$ which describes the low-frequency behavior of the density of states $N(\omega)$,

$$N(\omega) \sim \omega^{\tilde{d}_E - 1} ,$$
$$\tilde{d}_E = \frac{2D}{\tilde{\zeta}_E + D} . \tag{5}$$

For percolating clusters the expression for K in Eq. (3) together with the relation[15] $N_s(L) \sim L^{1/\nu}$ gives $\tilde{\zeta}_E = 2 + 1/\nu$.[7] Using $D = d - \beta/\nu$ we find

$$\tilde{d}_E = \frac{2(d\nu - \beta)}{(d+2)\nu + 1 - \beta} . \tag{6}$$

Thus, the elastic spectral dimension depends only on static exponents and not the conductivity exponent. The mean-field value of $\tilde{d}_E = 1$. For $d = 2$ and 3 the static results lead to $\tilde{d}_E \sim 0.8$ and 0.9, respectively. Thus, $N(\omega)$ for a percolating cluster at $p = p_c$ is slightly divergent as $\omega \to 0$. In contrast, $N(\omega) \cong \omega^{\tilde{d}-1}$ with $\tilde{d} \cong \frac{4}{3}$ for the Born model.[9]

The backbone of branched fractals such as DLA (Ref. 12) and cluster-cluster aggregates[13] contain no loops. The elastic properties can be thus obtained from Eq. (2), $K(L) \sim 1/(L^2 L^{D'})$. The fractal dimension of the backbone D' is larger than unity and smaller than the fractal dimensionality of the object. These bounds together with the relation $\tilde{\zeta}_E = 2 + D'$ give

$$\frac{D}{D+1} < \tilde{d}_E < \frac{2D}{3+D} . \tag{7}$$

Using the value of $D = 1.7$ for DLA in $d = 2$ (Ref. 12) we find $0.62 < \tilde{d}_E < 0.71$ in $d = 2$. Analogous arguments for the Born model give $1 < \tilde{d} < 2D/(D+1)$.[16]

We now describe our numerical technique to test the above scaling theory. To obtain the spectrum of vibrational states we (a) express the Hamiltonian H in Eq. (1a) in terms of the variables $\{\mathbf{u}_l\}$, the small displacements from the original lattice position, (b) set up $2N_c$ dynamical equations, where N_c is the number of sites on the cluster, and (c) Fourier transform these equations and write them in matrix notation: $\hat{\mathbf{A}}\mathbf{U} = \omega^2 \hat{\mathbf{I}}\mathbf{U}$. Here $\hat{\mathbf{A}}$ is a $2N_c \times 2N_c$ matrix and $\mathbf{U}$ is a vector describing the vibration amplitudes. The eigenvalues of $\hat{\mathbf{A}}$ can then be obtained numerically. A similar but somewhat simpler procedure is carried out for the Born model where $\hat{\mathbf{A}}$ is an $N_c \times N_c$ matrix.

Our results for the density of states $N(\omega)$ for percolating clusters for $d = 2$ at $p = p_c$ are shown in Fig. 1(a). The results are an average over three clusters of approximately 1000 sites each. The values of $G = 1$ and $Q = 100$ were chosen for the elastic constants since this choice assures that the lowest vibrational band consists of purely flexural modes. The density of states at low frequencies follows a power law $N(\omega) \propto \omega^{-a}$, where $a = 1 - \tilde{d}_E = 0.12 \pm 0.05$ down to a lowest frequency $\omega_{\min}$ determined by the finite size of the cluster. Figure 1(b) shows the integrated density of states[17] $I(\omega) \sim \omega^{\tilde{d}_E}$ from which one can determine $\tilde{d}_E$ more accurately. We obtain a value of flexural spectral dimensionality[18] $\tilde{d}_E = 0.82 \pm 0.05$. This value leads to the exponents $\tilde{\zeta}_E = 2.85 \pm 0.3$ and $\tau = \tilde{\zeta}_E \nu = 3.5 \pm 0.4$. Here τ is the exponent for the static elastic moduli κ near p_c: $\kappa \propto (p - p_c)^\tau$. This is the first numerical confirmation of the prediction of Ref. 7, $(\tau = 3.67)$.[19] For comparison we also plot the density of states of the scalar Born model averaged over three clusters of $N_c \sim 2100$. The difference in the

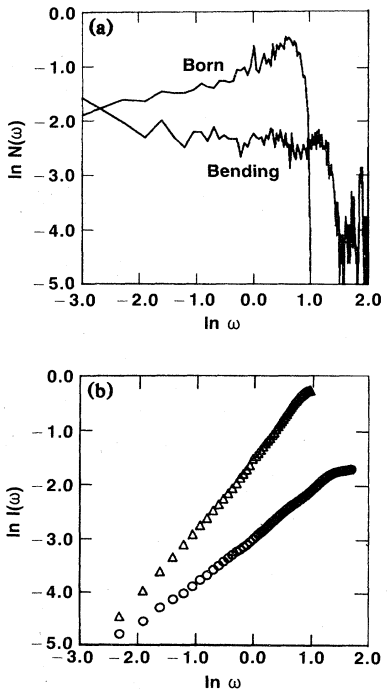

FIG. 1. (a) Density of states $N(\omega)$ vs frequency ω for the percolating clusters at $p = p_c$. The results are averaged over three clusters of average size 1018 for the bending case on a 44^2 square lattice and 2110 for the Born model on a 64^2 square lattice. (b) Integrated density of states $I(\omega)$ vs ω for the same clusters. Circles are for the bending model and triangles for the Born model.

density of states of the two models is clear. The scalar spectral dimensionality of $\tilde{d}$ obtained from the curves in Figs. 1(a) and 1(b) is 1.25 ± 0.10, consistent with the expected value of 1.32.

The results for the density of states for DLA clusters are shown in Fig. 2. The value of $\tilde{d}_E$ is 0.60 ± 0.05, which is consistent with the theoretical bounds given by Eq. (7). We also find $\tilde{d} = 1.10 \pm 0.05$ compared to a value of 1.35 ± 0.10 calculated from diffusion studies[20] and the theoretical upper bound of 1.26.

The most interesting aspect of these results is that a flexural spectral dimensionality that is smaller than unity dominates the low-frequency dynamical behavior of fractal structures. The results for the density of states of the two types of fractals analyzed here, though quite different from each other, are qualitatively quite similar, suggesting that this phenomena is rather general for fractal system. The divergence of the density of states leads to questions about the mechanical stability of fractal objects. Indeed our results imply that if the size of the object is sufficiently large so that the energy of the lowest mode falls below kT, the object will not retain its original shape and will become unstable with respect to thermal fluctuations. This condition sets an upper limit on the size of nonequilibrium fractal aggregates. Larger than this critical size, the aggregate configuration will be determined by relaxation to thermal equilibrium, much like in a large branched polymer, resulting in a crossover to a different fractal dimension.

Whether our theory applies to macromolecular systems such as gels and cross-linked rubber networks is still largely unanswered. The large-scale structure of these materials is determined by the balance of entropy and excluded volume interactions. It has been recently suggested[21] that in this case the presence of external forces such as the stress due to osmotic pressure, leads to a scalar type of elastic behavior. We may conjecture, however, that since macromolecules usually possess some rigidity over length scales smaller than the Kuhn persistence length[22] the flexural elasticity and dynamics should still play an important role. This observation is consistent with measurement of the elastic properties of polycondensed gels near the gel point,[23] which give $\tau = 3.0 - 4.0$ in agreement with the prediction of the flexural elastic model.

It would be very interesting to observe the dynamic behavior described above experimentally, in systems such as colloidal aggregates. This could be probably achieved by techniques such as forced Raleigh scattering or ultrasound absorption.

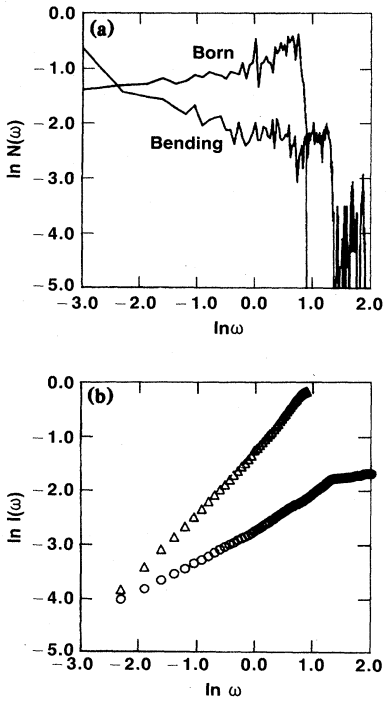

FIG. 2. (a) Density of states $N(\omega)$ vs frequency ω for the DLA clusters. The results are averaged over three clusters of size $N_c = 1000$ on a square lattice for bending and $N_c = 2400$ for Born model. (b) Integrated density of states $I(\omega)$ vs ω for the same clusters. Circles are for a bending model and triangles for the Born model.

We are grateful to Y. Kantor for generating the DLA clusters and to S. Alexander and Y. Kantor for helpful discussions.

[1] *Kinetics of Aggregation and Gelation,* edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).

[2] *Proceedings of the Third National Bureau of Standards Conference on Fractals,* edited by M. F. Schlesinger [J. Stat. Phys. **35** (1984)].

[3] *Carbon Black-Polymer Composites,* edited by E. K. Sichel (Dekker, New York, 1982).

[4] D. A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984).

[5] S. K. Sinha, T. Freltoft, and J. Kjems, in Ref. 1.

[6] D. W. Schaefer, J. E. Martin, P. Wiltzius, and D. S. Cannell, Phys. Rev. Lett. **52**, 2371 (1984).

[7] Y. Kantor and I. Webman, Phys. Rev. Lett. **52**, 1891 (1984).

[8] P. G. de Gennes, J. Phys. (Paris) Lett. **37**, L1 (1976).

[9] S. Alexander and R. Orbach, J. Phys. (Paris) Lett. **43**, L625 (1982).

[10] G. S. Grest and I. Webman, J. Phys. (Paris) Lett. (to be published).

[11] *Percolation Structures and Processes,* edited by G. Deutscher, R. Zallen, and J. Adler, Annals of Israel Physical Society, Vol. 5 (Adam Hilger, Bristol, 1983).

[12] T. A. Witten and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1982).

[13] M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Lett. **51**, 1123 (1983); P. Meakin, *ibid.* **51**, 1119 (1983).

[14] In higher dimensionalities additional angular variables are included in the Hamiltonian (see Ref. 7). The basic elastic properties remain analogous to the $d = 2$ case.

[15] R. Pike and H. E. Stanley, J. Phys. A **14**, L169 (1981); A. Coniglio, Phys. Rev. Lett. **46**, 250 (1981).

[16] T. A. Witten and Y. Kantor, Phys. Rev. B **30**, 4093 (1984); S. Halvin *et al.*, Phys. Rev. Lett. **53**, 178 (1984).

[17] The integrated density of states $I(\omega)$ was obtained by summing over the discrete bins of the density of states histogram, and correcting for the difference between a discrete sum and an integral.

[18] Finite-size affects were studied by examining smaller size samples,

which produces results for $\tilde{d}_E$ closer to 1. This means that the infinite system values of $\tilde{d}_E$ may be even slightly smaller than we find.

[19]After this paper was completed we received two preprints in which the value of τ was determined by numerical simulations of the static elasticity: $\tau = 3.5 \pm 0.2$ [D. J. Bergman, Phys. Rev. B **31**, 1696 (1985)] and $\tau = 3.2 \pm 0.5$ [S. Feng, P. N. Sen, B. I. Halperin, and C. J. Lobb, Phys. Rev. B **30**, 5386 (1984)].

[20]P. Meakin and H. E. Stanley, Phys. Rev. Lett. **51**, 1457 (1983).

[21]S. Alexander (unpublished).

[22]Paul J. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, 1953).

[23]M. Adam, M. Deslanti, D. Durand, G. Hild, and J. P. Munch, Pure Appl. Chem. **53**, 1489 (1981).