Can One "Hear" the Thermodynamics of a (Rough) Colloid?

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We calculate the effects of surface singularities, e.g., wedges, on the thermodynamics of electric double layers near a rough colloid or charged membrane. Each wedge yields an additive contribution to the free energy $\mathcal{F}$ that is a function of the angle. With a probabilistic Brownian representation of $\mathcal{F}$, we give a geometrical analysis of $\mathcal{F}$ entirely similar to that of vibration eigenmodes given by Kac in "Can one hear the shape of a drum?." Our analysis yields a universal scaling law for the free energy of a *fractal* colloid with its *Minkowski* dimension. The case of a colloidal random walk is derived from conformal invariance.

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The thermodynamics of colloidal particles[1] is especially interesting as the meeting point of electromagnetism and statistical mechanics. *Uncharged* objects interact by van der Waals forces,[2] and by Casimir effect or dispersion forces[3] at larger distance, due to thermal or quantum fluctuations of the electromagnetic vacuum. When *charged* (or held at fixed potentials), surfaces floating in an electrolyte[1,2] interact via the screened Coulomb potential, which may be coupled by specific boundary conditions to position or shape fluctuations, as in polyelectrolytes, colloidal crystals, or bilayer fluid membranes.

Surprisingly, most studies have considered only highly idealized and symmetric shapes for the colloids[1,4] or near-planar interfaces,[5] even for the linearized Debye-Hückel (DH) theory,[1,6,7] which is valid for sufficiently low surface potentials or charges[1] and characterized microscopically by a single parameter, the screening length $\lambda_{\mathrm{DH}}=\kappa^{-1}$.

Progress has been made recently,[8,9] for surfaces of arbitrary shapes or topology, when "multiple-scattering" techniques, originally devised for studying the distribution of modes in cavities,[10] or the Casimir effect of arbitrary shaped conductors,[11] were applied successfully to the DH theory of colloids. The free energy $\mathcal{F}$ of charged *smooth* surfaces was calculated formally, as well as the surface tension and smooth-curvature expansion of $\mathcal{F}$.

However, the above results do not apply when the surfaces become *rough* and develop singularities, like *wedges* or *wrinkles,* a situation which we address here, and which may be experimentally important for the *ripple* phase of fluid membranes.[12] For a *completely rough* colloid, i.e., with a fractal boundary, we also expect a new universal scaling behavior of the free energy $\mathcal{F}(\kappa)$ in terms of the "fractal dimension" of the surface.

For this, connections between the DH theory of colloids and that of wave or field equations in arbitrary geometries will be brought to light in this Letter. Eigenmode problems[10] have been shown long ago to have a nice *probabilistic* interpretation in terms of diffusion of random walks (RW), as in Kac's[13] study of the vibrations of a drum. Similarly, we describe here the double-layer free energy $\mathcal{F}$ in terms of (abstract) Brownian diffusion near its surface. *Wedge* contributions to $\mathcal{F}$ appear as analogous to corner problems in vibrating membranes.[13,14] Moreover, the exact scaling behavior of $\mathcal{F}$ for a fractal colloid is obtained from the RW representation, in harmony with some recent rigorous results[15,16] on the eigenmode distribution of a "fractal drum." The method also allows us to use conformal invariance in two dimensions, as made explicit here for a collodial RW.

We consider two physical cases: (i) *conducting* colloidal surfaces S, held at fixed potential $\phi|_S=\phi_0$, the Dirichlet (D) problem; (ii) *insulating* "opaque" boundaries[6,9] with fixed surface charge density σ_0, the Neumann (N) problem. A main tool is the Green's function satisfying in the bulk electrolyte the source equation

$$(\Delta-\kappa^2)G(rr',\kappa)=-\delta(r-r')\,, \tag{1}$$

and specific D or N boundary conditions (BC) for a point $r'\to\alpha$ approaching the surface S from the bulk volume V, respectively, $G_D(\alpha r,\kappa)|_S=0$ and $\partial G_N/\partial n_\alpha(\alpha r,\kappa)|_S=0$, where $\partial/\partial n_\alpha\equiv\mathbf{n}_\alpha\cdot\nabla_\alpha$ is the normal derivative, $\mathbf{n}_\alpha$ being the (inward) normal at point α. Notice that interior and exterior problems *decouple.*[9] To be definite, we consider hereafter the interior problem, i.e., a vesicle filled by an electrolyte. All results extend to the exterior problem.

The total electrostatic free energy reads $\mathcal{F}=Af$, where the amplitudes are respectively $A_D=-\varepsilon\phi_0^2\kappa^2/8\pi$, $A_N=2\pi\sigma_0^2/\varepsilon$, with ε the electrolyte dielectric constant, and where the reduced "free energies" f are expressed in terms of the Green's functions.[9] For the Dirichlet problem

$$f_D=-\kappa^{-2}\int_S dS_\alpha dS_\beta\frac{\partial^2 G_D}{\partial n_\alpha\partial n_\beta}(\alpha\beta,\kappa) \tag{2a}$$

or, from (1),

$$f_D=\int_S dS_\alpha\int_V d^3r\frac{\partial G_D}{\partial n_\alpha}(\alpha r,\kappa)\,, \tag{2b}$$

while for the Neumann case,

$$f_N=\int_S dS_\alpha dS_\beta G_N(\alpha\beta,\kappa)\,. \tag{3}$$

Wedge.—Consider a two-dimensional (2D) infinite wedge of apex angle γ, wetted inside by an electrolyte. The Green's functions can be calculated exactly as a rather intricate Kantorovich-Lebedev transform

$$G(z,z';\kappa)=\pi^{-2}\int_0^\infty dx\,K_{ix}(\kappa\rho)K_{ix}(\kappa\rho')g(\theta,\theta';x)\,, \tag{4}$$

where

$$g_{D(N)}(\theta,\theta';x)=\cosh(\pi-|\theta-\theta'|)x+\varepsilon_{D(N)}\frac{\sinh\pi x}{\sinh\gamma x}\cosh(\gamma-\theta-\theta')x+\frac{\sinh(\pi-\gamma)x}{\sinh\gamma x}\cosh(\theta-\theta')x,$$

$$\varepsilon_D=-1,\quad \varepsilon_N=+1\,,$$

in which, in complex notation, $z=\rho e^{i\theta}$, $0\le\theta\le\gamma$, and K is the usual modified Bessel function. By using integral properties of the latter, Eq. (1) can be checked directly, as well as D or N BC, depending on $\varepsilon_{D(N)}$. The form (4) is well suited to the computation of (2a) and (3). For the Dirichlet problem, we first integrate over ρ,ρ' and take into account all pairs of normal derivatives on both sides of the wedge. The resulting x integral is diverging, however, due to the infinite wedge. We subtract its value for a flat wedge $(\gamma=\pi)$ as a reference point. After a careful calculation, we obtain

$$\delta f_{w(D)}(\gamma)\equiv f_{\text{wedge}}\big|_\pi^\gamma=-(4/\kappa^2)I_D(\gamma)\,, \tag{5}$$

where I has the simple integral representation

$$I_D(\gamma)=\int_0^\infty dx\left[1-\frac{\tanh\gamma x}{\tanh\pi x}\right]. \tag{6}$$

Notice that I_D does not depend on κ anymore. Indeed, in two dimensions $\mathcal{F}\sim-\kappa^2 f$ is dimensionless and, since a wedge is scale invariant, $\kappa^2\delta f_w$ must be a function of γ only. A similar calculation for the (subtracted) Neumann free energy (3) leads to

$$\delta f_{w(N)}(\gamma)=-(4/\kappa^2)I_N(\gamma)\,, \tag{7}$$

where $I_N(\gamma)=\int_0^\infty dx[1-\tanh(\pi x)/\tanh(\gamma x)]$. Notice the interesting duality between the N and D cases, $I_N(\gamma)=(\pi/\gamma)I_D(\pi^2/\gamma)$. The wedge universal function I_D is represented in Fig. 1. For sharp edges, $\gamma\to 0$, it *diverges* as $I_D(\gamma)\sim(1/\gamma)\ln 2$. In both the D and N cases, the thermodynamics of electric double layers tends to *open* wedges. If the wedge is immersed in the same electrolyte on both sides one has to sum $\delta\mathcal{F}_w(\gamma)+\delta\mathcal{F}_w(2\pi-\gamma)$.

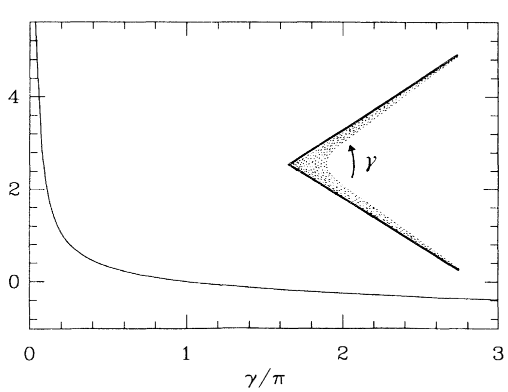

FIG. 1. Wedge contribution I_D, Eq. (6). For $\gamma/\pi\ge 2$, the values give $I_N(\gamma'=\pi^2/\gamma)$.

Smooth-rough surfaces.— Consider now a colloidal vesicle in three dimensions made of smooth ("analytic") patches, separated by sharp edges i, of angles γ_i and apex lengths L_i. In the strong-screening regime, $\kappa\to\infty$, contributions to the free energy become *local* and decompose into those of smooth parts and wedges. Hence the correct expansion of the reduced free energies (2),(3) for a *crumpled* membrane is

$$f=\kappa^{-1}\int_{\text{smooth } S}dS\left[1+\frac{a}{\kappa}H+\frac{b}{\kappa^2}H^2+\frac{c}{\kappa^2}K+\cdots\right]+\sum_{\text{wedges } i}L_i\delta f_w(\gamma_i)\,, \tag{8}$$

where the mean and Gauss curvatures are defined in terms of the principal radii of curvature R_1,R_2 as $H=\frac{1}{2}(1/R_1+1/R_2)$ and $K=1/R_1R_2$. The triads a, b, and c are universal dimensionless quantities, all associated only with the boundary conditions:[8,9] $(a,b,c)=(-1,-1,\frac{1}{2})$ (D) or $(1,\frac{3}{2},-\frac{1}{2})$ (N); δf_w is (5) or (7). In a real membrane, a ripple has a very small apex curvature radius r_0, and is seen as a wedge in the range $r_0\ll\lambda_{\text{DH}}=\kappa^{-1}\ll R_{1,2}$, where (5)-(8) apply, while it looks smooth at still higher electrolyte concentrations $\lambda_{\text{DH}}\lesssim r_0$. It is interesting to check that the linear curvature term $\kappa^{-2}\int dS\,aH$, e.g., in 2D, can also be reobtained by approximating a smooth surface by a polygon with vanishing edges $\gamma_i\to\pi$, and using (5) or (7). But wedge contributions cannot be obtained from the smooth-curvature expansion.

Random-walk representation.— It is well known that potential theory can be recast in terms of random walks. We make this point clear now for colloids, in the conducting and insulating cases simultaneously. Consider the time-dependent "heat kernel" $\mathcal{P}(t)=e^{t\Delta}$, with absorbing boundary conditions $\mathcal{P}_D|_S=0$, or reflecting BC $(\partial/\partial n_a)\mathcal{P}_N|_S=0$. It satisfies immediately[13] the Brownian diffusion or heat equation $(\partial_t-\Delta)\mathcal{P}=0$, with $\mathcal{P}(0)=1$. The "matrix element" $\mathcal{P}_D(rr',t)$ is simply[13] the probability density for a Brownian path to go from r to r' in time t, *without hitting the boundary.* The Neumann kernel $\mathcal{P}_N$ is that of a Brownian motion *reflected* at each contact at the boundary.[17]

Now, the Laplace transform of $\mathcal{P}$ is $\int_0^\infty dt\,e^{-\kappa^2 t}e^{t\Delta}=(-\Delta+\kappa^2)^{-1}$ as an inverse operator, and hence is exactly the Green's function G solution of (1), with proper BC. From this, we obtain immediately the free energies

(2),(3) under the form

$$f(\kappa)=\int_0^\infty dt\, e^{-\kappa^2 t}P(t)\,, \tag{9}$$

where in the Dirichlet case

$$P_D(t)\equiv\int_S dS_\alpha\int_V d^3r\frac{\partial}{\partial n_\alpha}\mathcal{P}_D(\alpha r,t) \tag{10}$$

is *the integrated probability that a random walk launched at* $t=0$ *anywhere inside the cavity hits the boundary for the first time at* t (Fig. 2); while in the Neumann case

$$P_N(t)\equiv\int_S dS_\alpha dS_\beta\mathcal{P}_N(\alpha\beta,t) \tag{11}$$

is exactly *the integrated probability that a reflected Brownian motion diffuses in time* t *between two arbitrary points of the boundary* (Fig. 2).

As a first application, we Laplace invert by (9) the $\kappa\rightarrow\infty$ expansion (8) of the colloid free energy to get new results on the *short-time* expansion of probabilities $P_{D(N)}$:

$$P(t)\underset{t\rightarrow 0}{=}\frac{\text{Area}}{\sqrt{\pi}}t^{-1/2}+a\int_S dS\,H-\sum_{\text{wedges } i}4L_iI(\gamma_i)+\frac{t^{1/2}}{\sqrt{\pi}}2\int_S dS(bH^2+cK)+\cdots\,, \tag{12}$$

where triads (a,b,c) and wedge contributions I depend on D or N boundary conditions as given above. In the opposite ("low salt") limit $\kappa\rightarrow 0$, some manipulations on (9),(10) give a very simple form to f in a power series of κ; e.g., in the fixed-potential case, $f_D(\kappa)=V\sum_{m=0}^{\infty}\langle t^m\rangle\kappa^{2m}$, where V is the (bounded) volume of the electrolyte, and $\langle t^m\rangle$ are moments of the *first exit time* t, averaged over random paths and initial points. In particular, $f(0)=V$; hence, $\mathcal{F}_D\cong-\varepsilon\phi_0^2V\kappa^2/8\pi$ for $\kappa\rightarrow 0$. The probability formalism also gives a *numerical* RW approach.[18]

Mostly studied, in mathematics[13,14,19] or in quantum chaos,[20] is the *trace* $Z(t)\equiv\text{Tr}e^{t\Delta}=\int_V d^3r\,\mathcal{P}(rr,t)$, i.e., the total probability of return of a (absorbed or reflected) RW. The singular corner contribution similar to (12) reads,[13] in 2D, $(\pi^2-\gamma^2)/24\pi\gamma$, and can be reobtained from conformal invariance,[21] suggesting a similar approach to our wedge result (6). Note that the free energies (9)-(11) can be finally expressed in terms of the eigenmodes $\{\lambda_n\}$ (the "vibrations of the drum") *and* of the eigenfunctions φ_n of $-\Delta$ (with D or N BC), since[13] $\mathcal{P}=\sum_n\varphi_n\otimes\varphi_n e^{-\lambda_n t}$; so, one can "hear" the colloid free energy, in the same way as its shape[13] through $Z(t)=\sum_n e^{-\lambda_n t}$.

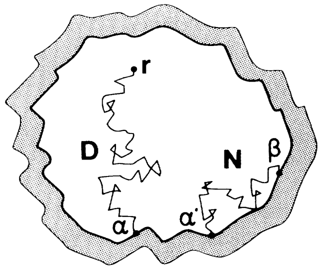

FIG. 2. D, random walks contributing to the first-hit probability (10) P_D; N, reflected surface-to-surface RW building up P_N (11) (for the interior electrolyte).

"Rectangular colloid."—A nice check of the above can be performed in 2D for a rectangular (colloid) box $[a'\times b']$. For, e.g., the Neumann case, a calculation of probability (11) from the eigenmode expansion yields typical Jacobi θ functions,

$$P_N(t)=4\frac{b'}{a'}\theta_{a'}(t)+4\frac{a'}{b'}\theta_{b'}(t)+8\,, \tag{13}$$

where

$$\theta_{a'}(t)=\left(\frac{a'^2}{4\pi t}\right)^{1/2}\sum_{p\in\mathbb{Z}}e^{-a'^2p^2/4t}\,,$$

after use of the Poisson summation formula. The colloid free energy (for the interior problem) is therefore the Laplace transform (9) of (13). The $t\rightarrow 0$ expansion of P_N is immediate: $P_N(t)=[2(a'+b')/\sqrt{\pi}]t^{-1/2}+8+\cdots$, up to exponentially small terms. This gives $f_N=L\kappa^{-1}+8\kappa^{-2}+\cdots$, where $L\equiv 2(a'+b')$ is the contour length, in agreement with (8) (taken in 2D), with zero curvature terms $H=0$, $K=0$ and *four* wedge contributions (7) $I_N(\frac{1}{2}\pi)=-\frac{1}{2}$.

Fractal colloid.—The RW representation is particularly useful for a colloid whose boundary is *fractal.* For the conducting case, $P_D(t)$ can be also viewed as the probability for a RW to *escape from the absorbing surface.* We expect the scaling law[22,23]

$$P_D(t)\sim\mathcal{A}t^{-(D_M+2-d)/2}\,, \tag{14}$$

where d is the space dimension, and $\mathcal{A}$ and D_M the fractal *Minkowski* measure and dimension of the boundary (not to be confused[23] with the Hausdorff dimension D_H). It is defined by

$$V_d(\varepsilon)\underset{\varepsilon\rightarrow 0}{\sim}\varepsilon^{d-D_M}\,,$$

where $V_d(\varepsilon)$ is the Euclidean d-volume of the points at a distance less than ε from the surface. There can be two different D_M depending on the side of the membrane. For electric double layers near a rough surface, this "layer dimension" is natural. In general, $d-1\leq D_H\leq D_M\leq d$. There is *no* rigorous proof of (14). For $D_M=d-1$, (14) coincides with the first term of (12). For a D-dimensional *crumpled* Gaussian manifold embedded in d-space, I find indeed an exponent $-\frac{1}{2}\varepsilon+O(\varepsilon^2)$, with $\varepsilon=2D/(2-D)+2-d\equiv D_M+2-d$; the $O(\varepsilon^p)$, $p\geq 2$, corrections should all vanish. When the fractal is itself a RW ($D_M=D_H=2$), (14) has been proven.[24] The best argument can be found in a conjecture by Berry[25] for the fractal boundary term in the density of modes of a domain V, made (rigorously) correct recently.[15,16] In terms of the "drum" partition function Z, it reads[16] (for the interior problem) $\bar{Z}(t) \sim t^{-D_{M,\mathrm{int}}/2}$, where $\bar{Z}(t) \equiv Z(t) - (4\pi t)^{-d/2} V$ is the difference from the *free-space Weyl* result.[13] $\bar{Z}(t)$ can be written as a convolution[15] of probabilities for hitting the boundary at least once and returning freely to the origin, and a scaling argument gives (14). From (9) follows the (total) free energy $\mathcal{F}_D$ of a fractal colloid at potential ϕ_0,

$$\mathcal{F}_D \sim -\phi_0^2 R^{D_M} \kappa^{D_M+2-d}, \tag{15a}$$

where we used $\mathcal{A} \sim R^{D_M}$ for a linear size R. For a fractal, no normals exist, but the *Neumann* problem can still be defined in a natural way.[26] Then the surface occupation probability scales as $P_N(t) \sim \mathcal{A} t^{-(d-D_M)/2}$, whence

$$\mathcal{F}_N \sim Q^2 R^{-D_M} \kappa^{d-D_M-2}, \tag{15b}$$

in terms of the total charge $Q = \mathcal{A}\sigma_0 \sim R^{D_M}\sigma_0$.

Koch curve and random walk as fractal colloids.—For the triadic closed Koch curve or snowflake,[27] we can see the emergence of (15) in 2D from (8). At the pth generation of equilateral triangles ($p=0$ corresponding to a single one of side R), the elementary length is $a_0(p) = R3^{-p}$ for each of the $N(p) = 3\times 4^p$ sides, separated by $\pi/3$ or $4\pi/3$ angles. For this polygon we get the asymptotic expansion (8),(5) $\kappa^2 f_D = (R\kappa)^{D_M} h(\kappa a_0)$, with $h(x) = x^{1-D_M} - c x^{-D_M} + \cdots$ for $x \to \infty$, and $D_M \equiv D_H = \ln 4/\ln 3$, $c = \frac{4}{3}[I(\pi/3) + 2I(4\pi/3)] \simeq 0.4810$. This result is valid for $\kappa a_0(p) \gg 1$, i.e., a very small Debye-Hückel screening length. When κa_0 crosses over to 1 (fractal regime), we expect h to become constant, in agreement with (15a).

Consider finally a fractal colloid mode itself of a RW, of fractal dimension $D_H = D_M = 2$, and length $\mathcal{S}$, with a mean size $R^2 \sim \mathcal{S}$. The probability P_D (14) is made up of the bulk contribution[25] $\sim \mathcal{S} t^{-(4-d)/2}$, and an *end effect* term $\sim a_0^{2\zeta+d-2} t^{-\zeta}$, where a_0 is a microscopic cutoff length, and ζ the *end* exponent governing the *nonintersection probability*[28] of two RW starting at a common origin. In 2D, we know from conformal invariance,[28] $\zeta = \frac{5}{8}$. By Laplace transform (9), we find in 2D the (quenched) free energy of a RW,

$$\mathcal{F}_D \sim \mathcal{S}\kappa^2 \ln \kappa a_0 + \mathrm{const} \times (a_0\kappa)^{5/4}. \tag{16}$$

The first term is extensive, but in the Coulombic regime $\kappa \to 0$ the end effects dominate, as expected, with a nontrivial conformal exponent $\frac{5}{4}$.

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[1] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948); R. J. Hunter, *Foundations of Colloid Science* (Clarendon, Oxford, 1987).

[2] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1985).

[3] H. B. G. Casimir, Proc. K. Ned. Akad. Wet B **51**, 793 (1948); H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).

[4] D. J. Mitchell and B. W. Ninham, Langmuir **5**, 1121 (1989); H. N. W. Lekkerkerker, Physica (Amsterdam) **167A**, 384 (1990).

[5] P. Pincus, J. F. Joanny, and D. Andelman, Europhys. Lett. **11**, 763 (1990).

[6] M. Winterhalter and W. Helfrich, J. Phys. Chem. **92**, 6865 (1988).

[7] R. E. Goldstein, A. I. Pesci, and V. Romero-Rochín, Phys. Rev. A **41**, 5504 (1990); D. Bensimon *et al.*, J. Phys. (Paris) **51**, 689 (1990).

[8] B. Duplantier, R. E. Goldstein, V. Romero-Ronchín, and A. Pesci, Phys. Rev. Lett. **65**, 508 (1990).

[9] B. Duplantier, Physica (Amsterdam) **168A**, 179 (1990).

[10] R. Balian and C. Bloch, Ann. Phys. (N.Y.) **60**, 401 (1970); **84**, 559 (1974).

[11] R. Balian and B. Duplantier, Ann. Phys. (N.Y.) **104**, 300 (1977); **117**, 165 (1978).

[12] J. A. N. Zasadzinski, J. Schneir, J. Gurley, V. Elings, and P. K. Hansma, Science **239**, 1013 (1988).

[13] M. Kac, Amer. Math. Month. **73S**, 1 (1966); see also M. E. Fisher, J. Combinatorial Theory **1**, 105 (1966).

[14] H. P. McKean and I. M. Singer, J. Differential Geometry **1**, 43 (1967).

[15] J. Brossard and R. Carmona, Commun. Math. Phys. **104**, 103 (1986).

[16] M. L. Lapidus and J. Fleckinger, C. R. Acad. Sci. Paris Ser. I **306**, 171 (1988); J. Fleckinger and D. G. Vasil'ev, *ibid.* **311**, 867 (1990).

[17] See, for instance, P. Hsu, Commun. Pure Appl. Math. **38**, 445 (1985).

[18] R. E. Goldstein, T. C. Halsey, and M. Leibig, preceding Letter, Phys. Rev. Lett. **66**, 1551 (1991).

[19] M. Berger, Proc. Symp. Pure Math. **27**, 129 (1975).

[20] N. L. Balazs, C. Schmit, and A. Voros, J. Stat. Phys. **46**, 1067 (1987).

[21] J. L. Cardy and I. Peschel, Nucl. Phys. **B300 [FS22]**, 377 (1988).

[22] M. Cates and T. A. Witten, Phys. Rev. A **35**, 1809 (1987); R. M. Brady and R. C. Ball, Nature (London) **309**, 225 (1984).

[23] J. F. Douglas, Macromolecules **22**, 3707 (1989); B. Sapoval, J. N. Chazalviel, and J. Peyriére, Phys. Rev. A **38**, 5867 (1988); A. Maritan, A. L. Stella, and F. Toigo, Phys. Rev. B **40**, 9269 (1989).

[24] G. F. Lawler, Israel J. Math. **65**, 113 (1989).

[25] M. V. Berry, in *Structural Stability in Physics*, edited by W. Güttinger and H. Eikemeir (Springer, Berlin, 1979); see also I. Stewart, Nature (London) **333**, 206 (1988).

[26] B. Simon (unpublished).

[27] B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1983).

[28] B. Duplantier and K. H. Kwon, Phys. Rev. Lett. **61**, 2514 (1988).