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Mechanical stability of tenuous objects

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Résumé. — Certaines structures de basse densité, telles que des amas colloïdaux, se déforment plus facilement lorsque leur taille augmente. Nous utilisons des propriétés d'homogénéité qui ont été récemment proposées afin d'étudier les effets dus aux fluctuations thermiques ainsi qu'aux forces de gravitation sur ces amas. Pour des amas colloïdaux typiques, formés de particules de taille 100 Å, le diamètre ne doit pas dépasser 10^3 à 10^4 fois celui des particules sans que se produisent des déformations importantes dues à ces deux effets. Les particules composantes de cette taille sont optimales : un important changement de taille quelconque rendrait l'amas moins stable.

Abstract. — Low-density structures such as colloidal aggregates become increasingly easy to deform mechanically as their size increases. We use recently-proposed scaling properties of such aggregates to investigate the effects of thermal fluctuations and of gravitational forces on such structures. For typical colloidal aggregates, made of 100 Å particles, the diameter may not exceed 10^3 to 10^4 particle diameters without significant distortion due to both thermal and gravitational effects. Constituent particles of this order of size are optimal : much larger or much smaller particles make mechanically less stable aggregates.

1. Introduction.

Certain random forms of matter, such as macromolecules in solution [1] or colloidal aggregates [2] have a wispy, tenuous structure. Their density is typically much smaller than that of the constituent material and appears to decrease indefinitely as their overall size increases. Yet the structures maintain their mechanical integrity; they support stress, screen hydrodynamic flows, and can transmit heat or electricity. The question naturally arises, how tenuous can such structures become before being compromised by their environment. That is, how low can the density become before the inevitable random forces acting on the object are sufficient to deform it appreciably.

In this note we investigate the effect of thermal vibrations and of gravitational stresses on some model structures thought to be similar to observed tenuous structures. We consider diffusion-limited aggregates [3] and cluster aggregates [4]. Similar reasoning would apply to rigid percolating clusters or random animals [5], but not to flexible objects like macromolecules. Our estimates rely on recently discovered scaling properties of these model structures. The structures appear to have the spatial scale invariance characteristic of a fractal : that is the average mass $M(L)$ within a distance L of an arbitrary point on the structure varies as a definite power L^D. The exponent D is known as the fractal dimension [6]. These objects cannot maintain their rigidity at non-zero temperature or in a non-zero gravitational field beyond some maximum size. The maximum depends on well-defined scaling properties of the geometric structure. The thermal stability improves if the objects are made with larger constituent particles. This may explain why observed rigid tenuous structures are made with constituents of a colloidal rather than an atomic scale. By contrast, the gravitational stability improves with smaller constituent particles. Thus a large aggregate must be made with particles which are neither too small nor too large if it is to be stable in both respects.

2. Thermal stability.

The thermal stability of an ordinary homogeneous solid may be readily expressed in terms of its elastic modulus κ [7]. If the matter at distance L from the origin is displaced by an amount u, this produces strains of the order $\varepsilon \cong u/L$. The strain costs an elastic energy whose density is $\kappa\varepsilon^2/2$. Elastic moduli in bulk matter are in the range of 2-50 eV per atomic volume [8]. At temperature T, thermal vibrations induce an average strain ε_T given by

$$k_B T \cong \kappa L^d \varepsilon_T^2 . \tag{1}$$

Here d is the dimension of space and k_B is the Boltzmann constant. (We note that this is the energy associated with the average strain, and it does not include the energy for local strains.) Thus in homogeneous solids the average strain fluctuates by an amount proportional to $L^{-d/2}$; overall distortions are smaller for larger objects.

In the tenuous structures of our study, a displacement u certainly does not produce a uniform density of strain energy. Instead, the strain energy depends on the large-scale geometry of the structure. The situation is similar for another fundamental response of the structure : the conductivity. For this latter case the response can be related [9] to the ant-in-a-labyrinth problem [10]. De Gennes has argued [11] that the elasticity of some tenuous structures scales with their conductivity. But de Gennes' reasoning does not apply to *rigid* elastic structures, and for these a different approach is needed. We consider first a branched structure such as that of diffusion-limited aggregates and cluster aggregates. In these structures, there is essentially only one path connecting any pair of constituent particles, as illustrated in figure 1. We imagine placing one of these particles at the origin and holding it fixed in position and orientation while the other is displaced by an amount u. For a branched structure, only the one-dimensional path connecting the two particles is strained. For distances L much larger than the particle size « a » the average number of particles in a connecting path, N_c, scales as some power of L ; we denote this power as D_c. The elasticity of branched aggregates is thus essentially that of contorted, rigid linear chains.

Such chains have been recently studied by Kantor and Webman [12]. They find that the displacement u under an applied force costs an energy E given by

$$E \sim [R_{\text{perp}}^2 N_c]^{-1} u^2 .$$

Here R_{perp}^2 is the squared radius of gyration of the path minus the squared radius of gyration of its projection on the direction of the applied force. If the applied force is in an arbitrary direction, R_{perp} is of the order of L. The coefficient of u^2 is the force constant associated with the displacement. We denote it as $K(L)$. Now, the thermal fluctuations of u have an energy E of order $k_B T$; thus,

$$\langle u^2 \rangle \cong [K(L)]^{-1} k_B T \cong (L/a)^2 N_c [K(a)]^{-1} k_B T .$$

Here $K(a)$ is the force constant for a pair of constituent particles. Its magnitude depends heavily on the strength of the bond between particles. For convenience we express $K(a)$ as a factor α times the force constant for deformation of a single particle, obtained from equation (1) above. The

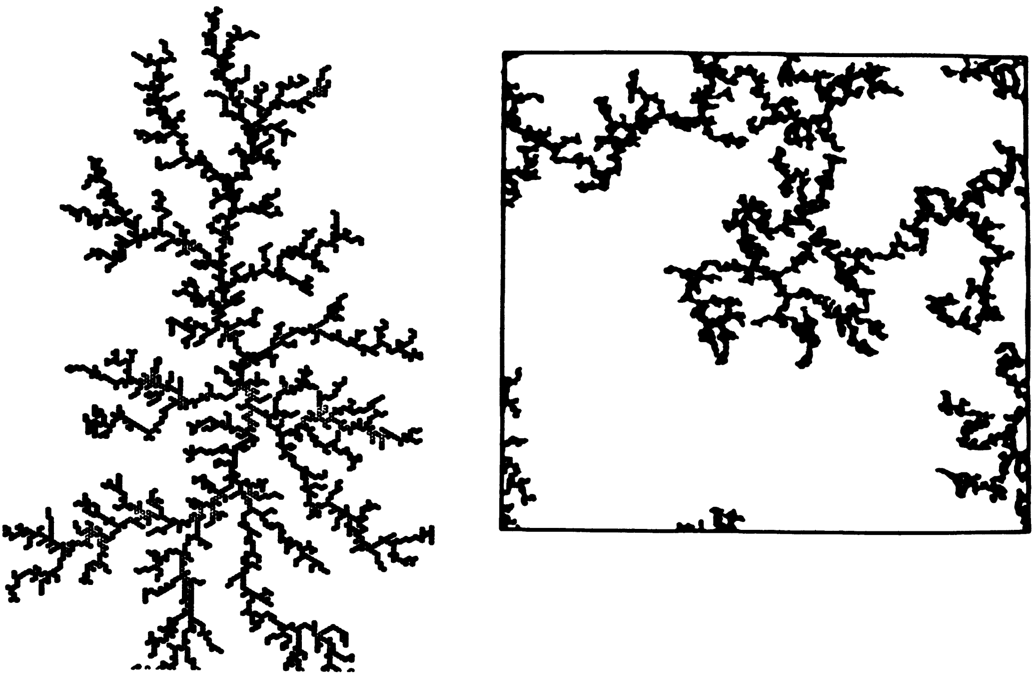

Fig. 1. — A diffusion-limited aggregate [3] (left) and cluster aggregate [4] (right) in two dimensions. The absence of loops on all but smallest scales is evident.

factor α accounts for the weak bonding between particles. It is much smaller than 1 for weakly bonded particles, and may approach unity for, e.g., welded metallic particles. Clearly the stability is reduced if α is decreased. We estimate that it is typically of order 10^{-1} or smaller. Thus for a single particle

$$E = [K(a)/\alpha]\, u^2 = \kappa a^d (u/a)^2 .$$

We may write the volume a^d as the volume per atom b^d times the number of atoms n in a particle. Then the mean squared strain may be compactly expressed as

$$\varepsilon_T^2 \cong \frac{k_B T}{\alpha \kappa b^d} \frac{N_c}{n} \cong \frac{k_B T}{\alpha \kappa b^d n} \left[\frac{L}{a}\right]^{D_c} .$$

As noted above, κb^d is in the range of 10 eV, while $k_B T$ is 1/40 eV at room temperature. Evidently the average strain increases with the length scale L. For sufficiently large L and N_c, the strain becomes of the order of unity. Aggregates larger than this become completely flexible, and are free to respond to internal forces like a flexible polymer. If these forces are attractive, the structure may attain a « collapsed » state of non-zero limiting density, as the size grows.

The range of rigid behaviour becomes narrower if the number of atoms per particle n is reduced. For colloidal particles n is 10^3 or more, and so the maximal value which can be attained by N_c before the thermal fluctuations distort the structure may be 10^4 or more. But for atomic-scale particles, with $n \cong 1$, N_c is only of the order of 10. This stabilizing effect of n may explain why the tenuous aggregates familiar in nature tend to be composed of particles of a colloidal scale or larger.

To make further predictions about thermal stability requires information about how N_c

scales with L. The power D_c describing this scaling has not been reported for either diffusion-limited aggregates or cluster aggregates. This D_c must be at least 1 to provide a connected path. Measurement of D_c by simulations would be very valuable.

Our approach can be readily extended to tenuous objects such as percolation clusters [5], which have more than one path connecting any pair of points. In that case D_c in the above expressions should be replaced by the exponent $\tilde{\tau} - d$, where $\tilde{\tau}$ defines the scale dependence of the effective bulk modulus :

$$\kappa(L) \sim L^{-\tilde{\tau}}.$$

In a branched structure which is sufficiently homogeneous, the exponent D_c may be related to the scaling of the conductivity, and thence to the spectral dimension [9, 13] $\tilde{d}$ of Alexander and Orbach. We have argued elsewhere [14] that the conductivity is determined primarily by linear, unbranched segments whose arc length is of the order of $N_c(L)$. Using standard relations [9, 13] for the conductivity in terms of D and $\tilde{d}$, we find $D_c = D(2/\tilde{d} - 1)$.

Using the simulation data of Meakin and Stanley [15] for diffusion-limited aggregates, we may get information about their D_c. The simulations yield $\tilde{d}$ values ranging from 1.1 to 1.45 in two dimensions, and from 1.2 to 1.64 in three. The fractal dimension D is about 1.7 in two dimensions and about 2.5 in three. Using these values we infer that $1 \leqslant D_c \lesssim 1.4$ in two dimensions and $1 \leqslant D_c \lesssim 1.67$ in three. These limits on D_c could be used to refine slightly our predictions for thermal stability.

3. Gravitational stability.

Another limit on the rigidity of an aggregate comes from gravitational effects. For an aggregate sedimenting under gravity, the weight force is compensated by hydrodynamic friction from the surrounding fluid. The weight acts uniformly throughout the aggregate, while the friction acts primarily at the surface. (The aggregates are dense enough to screen the hydrodynamic field [1].) For an aggregate of mass M and size L, the resulting force is of order Mg. (Strictly, M should be the mass of the aggregate less that of the displaced fluid.) The corresponding displacement u is of order $Mg/K(L)$. The ratio of gravitational strain $\varepsilon_g \equiv u/L$ to thermal strain *squared* is independent of the assumed elasticity $K(L)$:

$$\varepsilon_g \cong \varepsilon_T^2 \, MgL/(k_B T).$$

The factor on the right is the size L relative to the mean equilibrium height h for Brownian particles of mass M. Aggregates which attain a size h without becoming thermally unstable are ultimately limited by gravitational effects. The gravitational stability is not improved by making larger constituent particles. If the number of particles in the aggregate is N,

$$\varepsilon_g \cong \frac{mgb}{\kappa b^d} \, \frac{a}{\alpha b} \, \frac{L}{a} N N_c,$$

where m is the atomic mass. The first fraction arises from the constituent material. For gold [8] it is 3×10^{-16} ; for silica [8] it is 2×10^{-16}. The factor $a/\alpha b$ depends on the size of the constituent particles and on how strongly they are bonded together. For colloidal particles it is of order 10^2. The factor LNN_c/a depends on the amount of aggregation : it is unity for a single particle and scales as $(L/a)^{1+D+D_c}$.

For the aggregate to be gravitationally stable, the strain ε_g must be smaller than one. Using our estimates for gold or silica, this gives

$$\frac{L}{a} \lesssim [10^{14}]^{\psi},$$

where $\psi = 1/(1 + D + D_c)$. Using $D_c = 1$ and the D values given above we obtain $L/a \lesssim 10^3$ for diffusion-limited aggregates and 10^4 for cluster aggregates. If $D_c > 1$, the limit of stability is smaller. Aggregates much larger than the limit would sag into a pancake shape.

4. Conclusion.

Our limits for gravitational and thermal stability are rather similar in magnitude for typical colloidal aggregates, provided $D_c \cong 1$. Both effects set limits on L of roughly 10^3 to 10^4 particle diameters. This suggests that such typical particles are of optimal size; any large change in the radius a would reduce the limit of either thermal or gravitational stability. It appears [2, 17] that aggregates approaching these limits are actually produced in practice. Thus the prospects for extending the range of tenuous aggregates on earth greatly beyond what is presently known are distinctly limited.

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