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Fractal concepts and their applications to gels

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Abstract: Recent progress in the theory of fractal excitations, in the simulation of these excitations, and in experiments on fractal aerogels are reviewed. The paper is an extended abstract intended as a guide to the current literature.

Les progrès récents réalisés dans la description théorique de la dynamique des fractales, dans la simulation de ces excitations, et dans leur observation sur des aérogels de silice sont passés en revue. L'article est un résumé étendu destiné à servir de guide aux publications récentes sur le sujet.

Introduction

Fractal geometry [1] has found numerous applications in solid-state physics, in particular in the description of random systems and of properties near phase transitions. A large class of random systems, namely glasses, form the prime subject of this meeting. It has been proposed that the low temperature vibrational properties of glasses — and their peculiar thermal properties — could be explained if these materials were fractal over some length scale [2]. However, there is no known *structural* method that has been able to demonstrate unambiguously such a fractality, and the only “evidence” that could be presented so far on glasses invokes, one way or another, *spectral* properties. On the other hand the theoretical description of *fractons*, the vibrational eigenmodes of fractals [3, 4], required a number of non-trivial assumptions as explained below. For this reason, it is of current interest to review the scaling theory of fractons, and also to check how it applies experimentally, either in computer simulations of appropriate models, or in actual laboratory experiments. To provide real checks, it is important that the experiments be performed on systems that are *demonstrated* fractals, and therefore the experimental discussion concentrates on silica aerogels which form mass fractals, whose fractal dimension D , and fractal persistence length ξ can be determined independently of the dynamics by small-angle-scattering measurements [5, 6]. The material of this lecture draws heavily on collaborative work with several colleagues, especially

on Refs. 7 and 8. The experimental work has been performed jointly with the Laboratoire de Science des Matériaux Vitreux in Montpellier. The purpose of the following summary is to serve as guide to the current literature rather than as a paper in its own right.

2. The Dynamical Scaling Assumptions

The eigenmodes of strongly disordered fractals are expected to be well localized. They are called *fractons* [3]. For ordered fractals, even in presence of a certain degree of disorder [9], the situation is more complicated as different types of modes coexist over the same frequency interval [10]. This has even been recently tested experimentally for a one-dimensional case [11]. The discussion which follows is not addressed to ordered fractals, but rather to the strongly disordered limit. In practice, a material can only be fractal over lengths λ between the size of the constituting particles of diameter $\sim a$ and a fractal persistence length ξ . Beyond ξ the material is homogeneous. Practical limits on ξ are given by the size of calculations in numerical simulations, or by considerations of structural stability in laboratory experiments [12]. Over the fractal range, the average mass density of a mass fractal within a volume of size λ^d centered on a particle scales as

$$\rho \propto \lambda^{D-d}, \quad (1)$$

where D is the fractal dimension and d the Euclidean dimension of the embedding space. In the strongly disordered case, the localized fractons approximately corresponds to the same range of lengths, $a < \lambda < \xi$. The density of fraxon states per unit frequency interval is

$$N(\omega) \propto \omega^{\tilde{d}-1}, \quad (2)$$

where $\tilde{d}$ is a new dimension ($\tilde{d} \leq D$) which is called the spectral [4] or fraxon [3] dimension. The corresponding dispersion relation results from mode counting in fractal space, $d^D q \sim N(\omega) d\omega$, where q is a "wavevector" associated with fractons of average size λ , $q \sim \lambda^{-1}$. This gives

$$\omega \propto \lambda^{-D/\tilde{d}}, \quad (3)$$

for the average relation between fraxon "size," λ , and fraxon frequency ω .

The single-length-scale postulate for fractons is that all average lengths that can be defined on fractons, whether "wavelength," scattering length, localization length, or moments of the

wavefunction, do scale with the fracton frequency like Eq. (3), or in other words that all these lengths are the same within numerical constants [3, 7, 13]. This is a very strong statement which, like any dynamical scaling assumption, cannot be demonstrated at this stage of our theoretical knowledge, and thus needs to be checked by simulations or laboratory experiments.

The definition of the length λ in Eq. (3) requires a suitable averaging procedure. One knows from earlier simulations that different fractons of nearly the same frequency can have largely different spatial extent [14]. A proper statistical average can be defined in terms of the density-density correlation function [7]. One defines a density

$$\rho(\mathbf{r}, t) = \sum_i \delta(\mathbf{R}_i + \mathbf{u}_i(t) - \mathbf{r}) \quad , \quad (4)$$

where the summation is over particles (or sites, in simulations) at the equilibrium position $\mathbf{R}_i$, and with displacement $\mathbf{u}_i(t)$. The density is Fourier transformed and analyzed in modes $\mathbf{u}_\mathbf{q}$ of frequency $\omega_\mathbf{q}$, and Fourier amplitude $\rho^\alpha(\mathbf{q})$. The dynamical correlation function at $\omega \neq 0$ is given by [7]

$$G(\mathbf{q}, \omega) = \sum_\alpha \delta(\omega - \omega_\alpha) \rho^\alpha(\mathbf{q}) \rho^\alpha(-\mathbf{q}) \equiv \frac{kT}{\omega^2} g(\mathbf{q}, \omega) \quad , \quad (5)$$

to order $(\mathbf{q} \cdot \mathbf{u}_\mathbf{q})^2$. Equation (5) defines the reduced quantity $g(\mathbf{q}, \omega)$ from which the standard mode "quantization factor" kT/ω^2 , where kT is the thermal energy, has been factored out.

The single-length-scale postulate implies that also $g(\mathbf{q}, \omega)$ must scale only in terms of λ , and can be written, e.g. (in the isotropic case):

$$g(q, \omega) = q^y h[q\lambda(\omega)] \quad . \quad (6)$$

Here y is a scaling index and h is a scaling function. In the case of a homogeneous material, the quantity $g(q, \omega)$ can be expressed in terms of the strain fluctuations associated with the thermally excited phonons and it contains several lengths, such as the phonon wavelength λ and the phonon scattering length ℓ_{scat} , with $\lambda < \ell_{\text{scat}}$. For fractons, it also makes sense to define an associated strain. This can be done quite rigorously [7]. The *coherent part* of the average strain of a fracton, $\mathbf{e}^\alpha$, is only sensitive to the average relation between the vibrational amplitude $\mathbf{u}_\mathbf{q}$ and the positions within the fracton α . Averaged over many fractons, it is expected to scale as [7]

$$e(\omega) \propto \frac{u(\omega)}{[\lambda(\omega)]^\sigma}, \quad (7)$$

where $[u(\omega)]^2 \propto (kT/\omega^2) \lambda^{-D}$ is the average of the square of the thermal amplitude. The index σ is a new and independent scaling index, first defined in [13], with $\sigma \geq 1$. The case $\sigma = 1$ implies that the internal length within the vibrating blob of size λ is simply proportional to that size, just like in the homogeneous limit.

One must also note that the localization length, ℓ_{loc} , cannot appear in $G(\mathbf{q}, \omega)$ contrary to some statements published recently [15]. Localization is a more subtle property that can only be defined in terms of powers higher than 2 of the wave function, such as in the Thouless criterium for localization [16]. For fracton α , one writes:

$$\ell_{\text{loc}}^\alpha \equiv \left[\frac{\left[\sum_i |u_i^\alpha|^2 \right]^2}{\sum_i |u_i^\alpha|^4} \right]^{1/D} \quad (8)$$

It is that quantity which should also be proportional to the other definitions of λ .

3. Fracton Simulations

The early simulations [17] concentrated on the density of vibrational states, to determine $\tilde{d}$ from Eq. (2). They confirmed the Alexander-Orbach conjecture [3] that $\tilde{d} \simeq 4/3$ for all *percolation* models in *scalar* elasticity, independently of d and of the underlying lattice geometry. The simulations also revealed that $\tilde{d}$ is different from $4/3$ (and appreciably smaller) for tensorial elasticity models taking bond-bending into account. The difference between bond-bending and bond-stretching elasticities is at the origin of a crossover, as tenuous systems are dominated by the former at large scales and by the latter at small scales [18]. This crossover is also observed in appropriate simulations [19].

More recent simulations have started addressing questions beyond the value of $\tilde{d}$. The dispersion relation, Eq. (3), was verified for a scalar elastic model on site-percolation clusters [14]. Montagna *et al.* [15] defined a wavevector by the position in q of the maximum of $g(q, \omega)$, and they verified that the inverse of this wavevector also satisfies Eq. (3). However, they did not check the single-length-scale postulate, and concluded to the failure of scaling on other grounds.

The whole issue has been reconsidered in Ref. 8. It was found that *site*-percolation clusters of calculable sizes are in fact poor candidates for the simulation of fractal properties. The static

structure factor of these clusters does not show the expected q^{-D} power law over the required range of q , and the reason for this is a very strong "granularity" at short length scales. This arises from the random filling of sites with a probability p appreciably smaller than 1 (approximately equal to the percolation value p_c). The situation is much more favorable for *bond*-percolation clusters, which are practically free of this granularity effect. It was verified that the scaling relation, Eq. (6), applies well to these clusters, and that five different definitions of length [including two distinct ones related to Eq. (8)] all give a scaling of the form of Eq. (3). This is a very strong test of the single-length-scale postulate, which is thus fully vindicated for this particular model. Furthermore, the value of the strain exponent σ could be determined, and was found to be $\sigma = 1.05$ for $d = 2$, and $\sigma = 1.11$ for $d = 3$. Given these successes of the theory, it makes sense to also compare its prediction to actual experiments.

4. Experiments on Silica Aerogels

Silica aerogels are highly porous materials (their porosity can exceed 99%) which have remarkable mechanical and optical properties. Depending on details of the synthesis, they can form excellent fractals. Aerogels prepared by hydrolysis of silanes, followed by polymerization without the addition of a catalyst, form strongly ramified structures of rather tenuous particles; their fractal dimension is between 2.4 and 2.5. These materials are called "neutrally reacted." Aerogels prepared by polymerization in a basic environment (as they are still in the sol phase) are made of larger particles which aggregate in much more open structures, leading to a fractal dimension around 1.8, a value close to the one for diffusion-limited cluster-cluster aggregation. Such values are also obtained for colloidal aerogels prepared by aggregation of commercial suspensions of silica particles (Ludox) [20]. Using an appropriate preparation, in particular in the case of the neutrally reacted gels, it has been possible to obtain series of samples of different densities for which the value of D extracted from the whole series using Eq. (1) at $\lambda = \xi$ is the same as the value of D extracted from each individual sample by small-angle-neutron-scattering determination of the static structure factor $S(q) \propto q^{-D}$. Such samples are called *mutually self-similar* [6]. Ideally two mutually self-similar samples of different density could not be distinguished from each other when observed at scales where both are fractal. They only differ by the extent of their fractal range, that is by ξ .

Dynamical measurements on these aerogels have been performed by light scattering (Brillouin and Raman) and by inelastic neutron scattering using instruments of various resolutions (time-of-flight, backscattering and neutron spin echo). The main results have been reviewed recently elsewhere [21]. To summarize:

- Brillouin scattering has allowed us to observe the phonon-fracton crossover at scales near ξ [22]. Performing these experiments on a mutually self-similar series, the value of

D could be extracted from $\xi(\rho)$ [using Eq. (1) above], and the value of $\tilde{d}$ from the dispersion law at $\lambda = \xi$ [using Eq. (3) above]. The value of D was independently confirmed by small-angle-neutron-scattering [6] and that of $\tilde{d}$ by direct measurement of the density of states in the same frequency range by neutron spin-echo spectroscopy [23].

- Raman scattering, over the appropriate frequency range, has revealed a scaling regime corresponding to the entire fracton domain ($a \lesssim \lambda \lesssim \xi$) [24]. I return to this in the next section.
- Inelastic neutron-scattering performed over the same broad range of frequencies (from below 1 GHz to ~ 1 THz) revealed two different values of $\tilde{d}$ for a given sample, and different values of $\tilde{d}$ for different samples [25]. The crossover in $\tilde{d}$ is best explained by the dominance of bond-bending elasticity at relatively low frequencies, giving way to bond-stretching elasticity at the higher frequencies, as foreseen by Feng [18]. The results on different samples emphasize (if need be) that $\tilde{d}$ is not a universal exponent, but rather another dimension characterizing the particular fractal. As pointed out by Mandelbrot [1], an infinity of dimensions would be needed to fully describe a fractal.

5. Light Scattering over the Whole Fracton Regime

The question of the scaling in ω of the scattered light intensity was already raised in [26], although the corresponding measurements had apparently been made at frequencies above the mass fractal regime of aerogels. The first measurements performed within the proper frequency domain also demonstrated the dependence of the scaling range on ξ , showing clearly the onset of the fractal regime [24]. Great experimental care was needed to obtain meaningful results (for example careful oxidation of the samples to remove the organic radicals, and dehydration just before the experiment). The interpretation of the scaling exponents remain debated to this day. In a recent publication [15] it was even claimed that Raman intensities should not scale, "owing to their casual origin." As a matter of fact, provided a single scattering process dominates, one should really expect that in a situation with dilation invariance, and with the validity of the single-length-scale postulate, also the scattered intensity should scale with λ , and thus with ω .

The situation has been explored in Ref. 7. Several mechanisms can lead to light scattering. The direct effect of density fluctuations contributes only via octupolar radiation and could thus be rather weak. The dipole-induced-dipole mechanism introduced in this context in Ref. 15 and which gives dipolar radiation, can lead to both a coherent term (related to the coherent part of the strain) and an incoherent term which scales differently. Which term dominates could depend on the actual structure of the fractal. A calculation of the scattering produced by

this mechanism on *bond*-percolation clusters [8] revealed that the scattering is in fact extremely sensitive to granularity. On bond-percolation clusters the *coherent* strain was found to dominate, giving for the so-called "coupling coefficient" $C(\omega)$, related to the intensity $I(\omega)$ by

$$I(\omega) = (kT/\omega^2) N(\omega) C(\omega) , \quad (9)$$

the following scaling relation:

$$C(\omega) \propto \omega^{(2\tilde{d}/D)(d+\sigma)-3\tilde{d}} . \quad (10)$$

This scaling exponent is in agreement with the simulation results [8]. A very different scaling is observed on *site*-percolation clusters [8, 15]. Another mechanism that could lead to light scattering is the fluctuation of the particle polarizabilities owing to the strain in these particles (Pockel's effect). Interpreting the results on aerogels [24, 25] with the coherent dipole-induced-dipole mechanism, one finds $\sigma \simeq 1$ [21]. This appears to be a reasonable result, since one certainly expects the internal structure of aerogels to be much more connected than that of percolation clusters. More work will be needed, in particular to estimate the relative strength of the various mechanisms in actual experimental situations.

In conclusion, the theory of fractal vibrations has been placed on a firmer footing, and some of the fundamental hypotheses have been tested by simulations. Further, experiments have demonstrated the relevance of this theory to appropriate forms of silica aerogels. Many thanks are expressed to my co-workers, named in Refs. 7, 8, 22, 23 and 25, for the invaluable contributions they have made to this development.

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