Absence of Definite Scaling Laws in Raman Scattering from Fractals

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The frequency dependence of the Raman coupling coefficient $C(\omega)$ is calculated numerically for square and cubic percolation clusters. No general scaling law in terms of the macroscopic parameters such as the fractal ($D$) and fracton ($d$) dimensions is found. $C(\omega)$ is sensitive to the microscopic structure of the clusters and depends on: site- or bond- percolation, presence or absence of dangling bonds, scattering mechanism and polarization, presence or absence of polarizability disorder. This situation makes the derivation of macroscopic parameters from Raman experiments unreliable.

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The properties of fractal objects are continuing to attract much interest from both the experimental and theoretical standpoint. Besides being interesting on their own, fractals are thought to be reasonably representative and relatively simple models of important classes of real disordered materials especially as regards the vibrational characteristics of the latter systems, and this probably explains why their dynamics has been so attractive to theoreticians. It is by now accepted that the statistically self-similar, static mass- or bond-distribution of disordered fractals (of which percolation clusters are the prototypes) is paralleled by peculiar dynamical characteristics. For example, the density of vibrational states follows a power law of the type $\rho(\omega) \propto \omega^{-d-1}$, where $d = 4/3$ for percolators) is called spectral dimension. Another quite general property of fractals is that their vibrational eigenstates (fractons) are localized: if one takes a frequency interval $\delta \omega$ and averages the localization lengths of the fractons whose energy lies in the interval $\omega \pm \delta \omega$, one finds that the average localization length varies as $l(\omega) \propto \omega^{-7/D}$, where $D$ is the fractal dimension. Although one should be extremely cautious in using average quantities such as $l(\omega)$, it is not unreasonable to expect that knowledge of $\rho(\omega)$ and $l(\omega)$ could help a lot in obtaining information on, for example, thermal conductivity in fractals and -possibly- in real disordered materials.

Unfortunately neither $l(\omega)$ nor the low-frequency $\rho(\omega)$ are directly and easily accessible to experiment in real disordered materials so that indirect measurements of these quantities might be of great help. If the above power laws were valid, this could be achieved by measuring $d$ and $D$. In this letter we will discuss Raman scattering; there are at least two good reasons why people have concentrated on this technique: (i) it is experimentally easy and does not require big facilities, and (ii) since we are dealing with disordered systems, and contrary to the case of crystals, all the eigenmodes contribute to the scattering. The price to be paid is that the (Stokes) scattered intensity in the harmonic approximation is given by:

$$I(\omega) = (n(\omega) + 1)\rho(\omega)C(\omega)/\omega$$

(1)

where $n(\omega)$ is the Bose-Einstein population factor for fractons and $C(\omega)$ is an average light-vibration coupling coefficient whose value depends on how the polarizability of the units (atoms or molecules) which constitute the system is modulated by the vibrational modes with frequency in the interval $\omega \pm \delta \omega$. Its $\omega$-dependence is not known a priori. So one important question is: is it possible to cast $C(\omega)$ in a form similar to $l(\omega)$ and $\rho(\omega)$, i.e. $C(\omega) \propto \omega^x$, ...
and is it possible to express $x$ in terms of $\overline{d}$, $D$ and maybe other parameters (which in the literature have been given in different times the names of $d_2$ and $\sigma$)? Or, in other words, is the Raman coupling coefficient a scaling quantity?

There have been several proposals for $x$, all of which were derived under the assumption that it is possible to determine $C(\omega)$ by considering scaling relations of the fracton-induced strain. In two recent papers we argued against such possibility on the basis of our numerical calculations of $C(\omega)$ in two- and three-dimensional (hereafter 2D and 3D respectively) site-percolation clusters which showed that (i) none of the proposed $x$ expressions could fit the numerical data in 2D and (ii) a single $x$ is not sufficient in 3D.

In the present letter we extend the previous work to several other kinds of 2D and 3D percolation structures: bond- and site-percolation (BP and SP respectively) with and without dangling bonds; we also investigate the effect of varying the scattering mechanism: full dipole-induced-dipole (FDID), DID restricted to nearest neighbors (NNDID), bond-polarizability (BPOL) Finally we look at the effects produced by changing the bare electric polarizabilities of the scattering units (electrical disorder, which was not introduced in previous works).

What we find is that $C(\omega) \propto \omega^6$ is a good representation of the numerical data only for BPOL in 2D and 3D and maybe for DID in 2D; in the latter case however $x$ depends on the specific system considered. $C(\omega) \propto \omega^6$ does not seem to work for DID in 3D. Our results also demonstrate beyond any doubt that the mechanical properties of a system (i.e. its mass distribution and the detailed shape of its vibrational eigenvectors) are not sufficient in general to determine $C(\omega)$.

These conclusions are at complete variance with those of a recent letter, whose authors propose another scaling law for $C(\omega)$ in terms of the mechanical parameters mentioned above ($\overline{d}$, $D$ and $\sigma$) and claim that this law compares well with their numerical results relative to BP clusters with dangling bonds.

The numerical procedures were the same as described in Refs. 3 and 4; the clusters contained identical masses ($M=1$) and spring constants ($K=1$), scalar elasticity was assumed. The average over many fractons is essential because the disorder-induced light scattering is an intrinsically fluctuating quantity and the accuracy in the determination of $C(\omega)$ depends on the number of modes present in each frequency interval. The most critical region is the low frequency one because of the low density of states and the big dimensions of the clusters needed. We overcame the problem of computation time and memory requirements by calculating only the low frequency modes of large clusters, while all the modes of smaller clusters were used for the intermediate and high frequency ranges. For instance, the result for SP 2D (two bottom traces of Fig. 1) is obtained by averaging: all modes of a $25 \times 25$ cluster (average over 200 realizations), the 200 lowest energy modes of a $50 \times 50$ cluster (50 realizations), the 400 lowest energy modes of a $65 \times 65$ cluster (20 realizations) and the 200 lowest energy modes of an $85 \times 85$ cluster (10 realizations).

It is very interesting to note in Fig. 2 (3D FDID) the important differences existing between systems with and without dangling bonds. Dangling bonds tend to put into electromagnetic contact regions which are dynamically uncorrelated (i.e. borders of fjords and similar areas) and, thus, to increase the FDID scattering mainly in the low-frequency (and low-intensity) range. The role of electromagnetic pair interaction between units which are spatially near but mechanically far apart has been used to explain the difference between FDID and NNDID in SP. This effect is not present in BPOL where the examined systems have very similar behaviors and follow the $\omega^6$ law in a very broad range both in 2D ($x \approx 1.3$) and in 3D (Fig. 3, $x \approx 1.6$). The authors of ref. 11 found no relevant difference between BP FDID and BP NNDID and we find the same result; but in the case of BP clusters what is meaningful is the comparison between FDID and BPOL. In fact, while SP BPOL and SP NNDID are the same thing, this is not true for BP: here nearest neighbor units can be found which are not bound, so that most of the above mentioned electromagnetic pair interaction is already present in NNDID.

We also observed tangible though minor differences between VV and VH polarizations in FDID for all kinds of clusters.

All these considerations show that there is an important local contribution to $C(\omega)$ because globally equal but locally different clusters produce different $C(\omega)$'s. This suggests that simple scaling arguments are unlikely to apply to this quantity. This view is strengthened by inspection of Fig. 4 which is relative to clusters whose units have been randomly assigned the bare polarizability values $\alpha_1$ and $\alpha_2$ with equal probabilities. The clusters which produce the three traces of Fig. 4 are the same, yet they yield different values of $x$, i.e. different "scaling laws" are found for the same mechanical system with the same scattering mechanism. Similar results are found for BPOL: introduction of the same electrical disorders as in Fig. 4 changes the slope from $x \approx 1.3$ to $x \approx 1.9$, a value very close to that of homogeneous systems.

The reason why $C(\omega)$ depends so markedly on the microscopic electrical and mechanical details of the system is to be found in the very nature of Raman scattering. Disordered systems scatter macroscopically because disorder does not allow the waves scattered by different units to interfere so as to cancel exactly the scattered amplitude as happens in crystals. In other words, Raman scattering is due to fluctuations, i.e. it is the mean square deviation of a zero-average quantity. It is not surprising that what is not exactly annulled by the interference process (i.e. the intensity at a given frequency) depends on the mechanical and electrical detailed structure and on how the respective disorders correlate.
Raman scattering has been used in recent literature in order to determine the mechanical parameters $d$, $D$ and $d_\phi$ or $\sigma$ of real systems by comparing the assumed functional form of the exponent $x(d, D, d_\phi, \sigma)$ to the "observed" $C(\omega)$. On the basis of the present results it appears that such procedure is devoid of any significance.

Whether or not it will be possible to derive reliable expressions for $C(\omega)$ is of course still an open question; the numerical results seem to suggest that a power law works in some cases (BPOL) and two different slopes are present in other cases, while in a few other instances this functional form seems to be pretty inadequate. Even in BPOL we find $x_{2D} < x_{3D}$, contrary to what is expected on the basis of the scaling models proposed so far.

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[12] See ref. 9 for a deeper discussion of the DID and BPOL mechanisms.
[13] The authors of Ref. 11 assert that BP clusters should always be preferred to SP in checking scaling properties; this proclamation is curious enough because from their Fig. 4 it appears that 3D SP follows their eq. (3) much more closely and in a broader frequency range than 2D and 3D BP, which look rather roundish (see also Figs. 1 and 2 of the present letter). Their conviction might be explained by the fact that fitting 2D SP, which has $x \approx 1$ (see Refs. 3 and 9), would require an unpalatable $\sigma \approx 1.5$. See Refs. 3 and 9 also for a different explanation of the presence of two slopes in 3D SP. In any case, for the reasons explained in the text, we believe that there is not much sense in eq. (3) of Ref. 11; among others, in the limit $d = D = 3$, $\sigma = 1$ (i.e. a homogeneous connected system) it leaves us with the eccentric value $x = -1$ instead of $x = 2$.
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[15] P. Benassi, O. Pilla, V. Mazzacurati, M. Montagna, G. Ruocco and G. Signorelli, Phys. Rev. B 44, 11734 (1991), discussed the effect of various kinds of electrical disorder on $C(\omega)$ in topologically perfect crystals, and found that it strongly depends on the site polarizability distribution.
[16] Of course, what is actually observed is the product $C(\omega)\rho(\omega)$, eq. (1), and in order to extract $C(\omega)$ one must either make assumptions on $\rho(\omega)$ as described at the beginning of this paper, or measure it by neutron scattering, but the range of frequencies where real solids are expected to be fractal is very low.