

Fractal vibrational excitations in polymers

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Low-energy fractal vibrational excitations in polymers have been studied by the methods of inelastic scattering of neutrons and Raman scattering. The spectral dimension of fractons $\bar{d} = 1.8$ and the superlocalization parameter $d_\phi = 1.5$ have been determined.

The study of the dynamic properties of fractal systems, in particular, the behavior of vibrational excitations (fractons) which are localized at the fractals, has recently elicited considerable interest. The density of states of fractons is determined by the spectral dimension¹ \bar{d}

$$g(E) \propto E^{\bar{d} - 1}, \quad (1)$$

while the wave function depends on the so-called superlocalization index,^{1,2} $d_\phi \gtrsim 1$:

$$\psi(\mathbf{r}) \propto l_\omega^{-D/2} \exp[-(\mathbf{r}/l_\omega)^{d_\phi}]. \quad (2)$$

Here D is the fractal dimension, and l_ω is the localization length of a fracton of frequency ω . The use of several experimental procedures has made it possible to estimate \bar{d} in some fractal entities.^{3–6} The superlocalization parameter d_ϕ , however, has been studied not nearly as extensively: There are no reliable experimental data, and only 2D systems have been modeled on a computer. The two studies^{7,8} which have been published show a considerable discrepancy in the values of d_ϕ .

In the present letter we present the results of an experimental study of fractal vibrational excitations by the method of inelastic neutron scattering and Raman effect. The first method makes it possible to measure the density of the vibrational states and, hence, to determine the spectral dimension of fractons, \bar{d} . The second method yields information on the wave function of fractons (2), i.e., on the parameters, \bar{d} , d_ϕ , and D . The combination of these two experiments has made it possible to determine the superlocalization parameter d_ϕ .

As the object to be studied we chose polymethylmethacrylate (PMM), a compound which, like all disordered polymers, has a fractal structure.⁹ Film samples of PMM were synthesized by a method which is described in detail in Ref. 10.

The neutron scattering spectrum was measured by using the time-of-flight method at scattering angles 30, 45, 60, 75, and 90°. The results were analyzed by following the usual procedure with allowance for all necessary corrections.¹¹ In the incoherent approximation we can reconstruct directly from the neutron experiment, without invoking model-based representations, a so-called generalized vibration spectrum $\theta(E)$

which is related to $g(E)$ by the relation

$$\theta(E) = \sum_i \sigma_i c_i M_i^{-1} |\mathbf{e}_i(E)|^2 \exp(-2W_i) g(E). \quad (3)$$

Here σ_i , M_i , c_i , and \mathbf{e}_i are the scattering cross section, the mass, the concentration, and the vibration vector of the atoms of the i th species, and W_i is the Debye-Waller factor. At $E < 5.5$ meV an average was taken over the momentum transfer in the interval between 1 and 3 \AA^{-1} . The depolarized Raman spectrum was measured in the 90° scattering geometry, using the DFS-24 apparatus at a spectral gap width of 1.5 cm^{-1} and excitation wavelength $\lambda = 647 \text{ nm}$. All measurements were carried out at room temperature.

Figure 1 shows the low-energy spectra $\theta(E)$ and Raman scattering normalized to the Bose intensity factor. Analysis of the spectra in log-log coordinates (Fig. 2) shows that it has a power-law region E^μ in an appreciable energy interval, from 2 to 10 meV. In the case $\theta(E)$ the slope is $\mu = 0.8 \pm 0.05$, and for Raman scattering it is $\mu = 0.7 \pm 0.15$. This part of the spectrum corresponds to the fracton region of the vibrational excitations. A comparison of μ with (1) for $\theta(E)$ makes it possible to estimate the spectral dimensionality of fractons in the test sample: $\bar{d} = 1.8$.

To interpret the data for Raman scattering, we need a theory of inelastic scattering of light on fractons. We are proposing a continual model which we briefly describe below. The matrix element M_i of the interaction of light with a fracton which is localized at the point r_i is determined by the gradient of the wave function at the fractal:

$$M_i \propto \int d^D r \nabla \psi(|\mathbf{r} - \mathbf{r}_i|) \exp(i\mathbf{q} \cdot \mathbf{r}). \quad (4)$$

In (4) $\mathbf{q} = |\mathbf{k} - \mathbf{k}'|$, where \mathbf{k} and \mathbf{k}' are the momenta of the incident and scattered

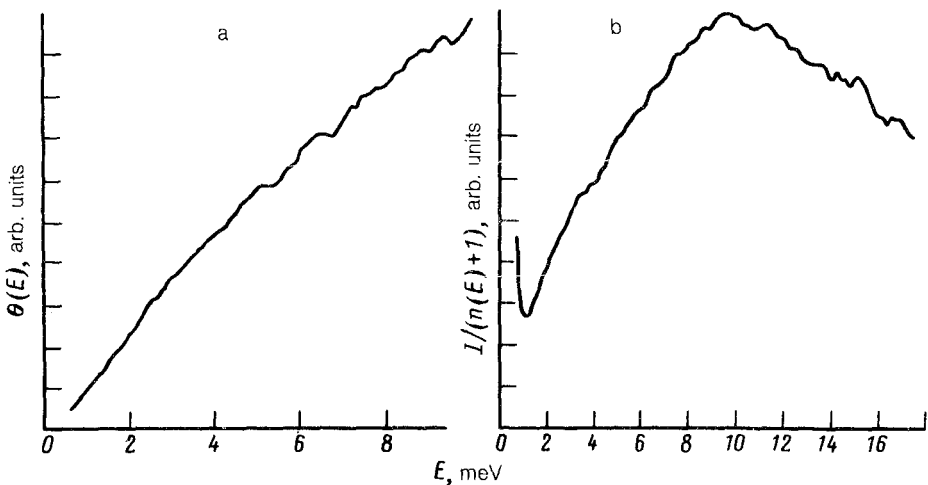


FIG. 1. Low-energy spectra of PMM films at $T = 300 \text{ K}$. a—Neutron data; b—Raman spectrum.

photon. In the integration range we have $gr \ll 1$. From (2) and (4) we find $M_i \propto l_\omega^{(D/2) - d_\phi} \exp(i\alpha_i)$, where α_i is the random phase. The square of the matrix element, summed over all fractons, depends on the correlation properties of the phase factor:

$$M^2 \propto \sum_{i,j} \exp(i\alpha_i) \exp(-i\alpha_j). \quad (5)$$

We can single out two cases: 1) Incoherent vibrations, $\langle \exp[i(\alpha_i - \alpha_j)] \rangle = \delta_{ij}$. In this case $M_{\text{incoh}}^2 \propto l_\omega^{D - 2d_\phi}$. 2) The radius of vibration coherence is on the order of the localization length of fractons, l_ω . In this case the sum in (5) is proportional to l_ω^D and $M_{\text{coh}}^2 \propto l_\omega^{2D - 2d_\phi}$. Since $l_\omega \propto \omega^{-\bar{d}/D}$ for fractons¹ and making use of the Fermi golden rule with $g(E)$, from (1) we find for the Raman scattering intensity normalized to the Bose factor: $I/(n+1) \propto E^\mu$, where $\mu = (2\bar{d}d_\phi/D) - 2$ in the incoherent case and $\mu = (2\bar{d}d_\phi/D) - (\bar{d} - 2)$ in the coherent case. Substituting into these expressions the experimental values $\mu = 0.7$ (Fig. 2) and $\bar{d} = 1.8$ and taking into account that $D \approx 2$ for the polymers,⁹ we find the superlocalization index d_ϕ : $d_\phi^{\text{incoh}} = 1.5$ and $d_\phi^{\text{coh}} = 2.5$. The correct value of d_ϕ can be chosen from these two values on the basis of the results of Ref. 12, where the Raman scattering method was used to determine the parameter d_s , which couples the Euclidean distance r and the shortest path between two points on the fractal, $l/l_0 \propto r^{d_s}$. The parameter values d_ϕ and d_s must be approximately equal in the case of exponential damping of the wave function of a fracton along the fractal: $\psi \propto \exp(-l/l_0)$ [compare with Eq. (1)]. Although exactly how d_s is related to d_ϕ is not known, the condition $I \lesssim d_\phi \lesssim d_s$ holds.² According to Ref. 12, the value of d_s for silica gel, where the parameters \bar{d} and D differ only slightly from the polymers, is 1.5,

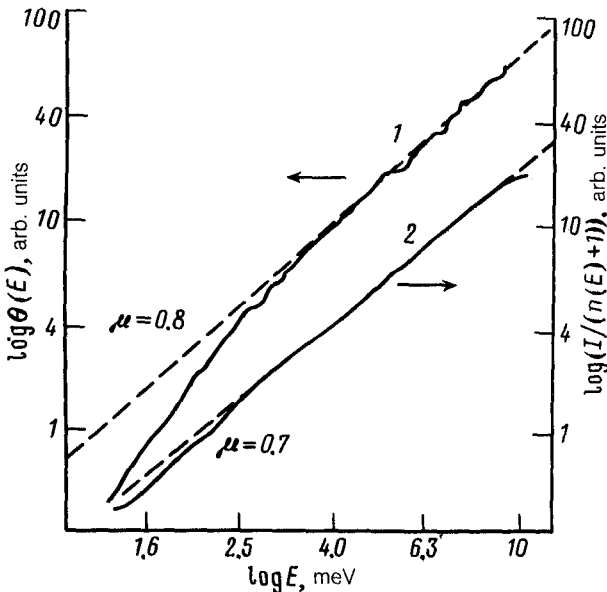


FIG. 2. Density of states (1) and intensity of Raman light scattering (2) in log-log coordinates.

in good agreement with our value for d_{ϕ}^{incoh} . This shows that the fractons are incoherent in a disordered polymer. We note that the expression for μ^{incoh} , which was obtained in Ref. 13, yields $d_{\phi} \approx 0.5$, suggesting that this expression cannot be used for polymers.

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- ¹S. Alexander and R. Orbach, *J. Phys. (Paris)* **43**, L625 (1982).
- ²S. Alexander *et al.*, *Phys. Rev. B* **32**, 6447 (1985).
- ³E. Courtens *et al.*, *Europhys. Lett.* **6**, 245 (1988).
- ⁴A. J. Dianoux *et al.*, *Phys. Rev. Lett.* **58**, 886 (1987).
- ⁵A. Boukenter *et al.*, *J. Phys. C* **21**, 541 (1988).
- ⁶U. K. Malinovsky *et al.*, *Chem. Phys. Lett.* **143**, 111 (1988).
- ⁷K. Yakubo and T. Nakayama, *Phys. Rev. B* **40**, 517 (1989).
- ⁸P. Uries *et al.*, *Phys. Rev. Lett.* **62**, 2515 (1989).
- ⁹P. Wiltzius, *Phys. Rev. Lett.* **58**, 710 (1987).
- ¹⁰V. A. Bagryanskiĭ and V. A. Tolkachev, *High Molecular Compounds B* **29**, 909 (1987).
- ¹¹M. G. Zemlyanov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **42**, 176 (1985) [*JETP Lett.* **42**, 217 (1985)].
- ¹²E. Courtens and R. Uacher, *Proceedings Roy. Soc. London A423*, 55 (1989).
- ¹³A. Boukenter *et al.*, *Phil. Mag. B* **59**, 125 (1989).

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