Quasielastic incoherent scattering in fractal systems

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The diffusive behavior of particles can be studied with the help of quasielastic light or neutron scattering. Diffusion within a fractal space does not follow the normal law $\langle r^2 \rangle \sim t$, r being the displacement in time t. In this paper we study quasielastic scattering in fractal spaces and try to predict new features which may be observed experimentally. Examples of such systems may be the AgI percolation clusters in glassy AgI borate and phosphate superionic conductors, gel-type protonic conductors, and biological systems. For such fractal systems our calculated line shape of scattered intensity, $S(\mathbf{k},\omega)$, is found to be oscillatory in nature unlike the Lorentzian centered at $\omega=0$, for normal diffusion. The maximum scattered intensity $S(\mathbf{k},0)$ has a power-law dependence on $\mathbf{k}$. Also the half width at half maximum is found to be independent of $\mathbf{k}$.

I. INTRODUCTION

Naturally occurring systems ranging from coastlines and cloud formations to porous rocks, capillary blood vessels, and the interior space within liposomes are at present being modeled as fractals.[1] For macroscopic objects, identification of the fractal nature is relatively easier. Standard methods are prescribed for determination of the fractal dimension. For microscopic objects the situation is more complex. Indirect methods are necessary and often it is possible to interpret the same data using alternative models, fractal and nonfractal. So it is desirable to obtain evidence of fractality from as many different sources as possible. An added complication is that real objects are not deterministic fractals like the well-known Koch curve or Sierpinski gasket, but are statistical fractals and exhibit a fractal nature only within a certain range of length scales.

For the study of microscopic systems, light, x-ray, or neutron scattering techniques are normally employed. Small-angle neutron scattering[2] has been extensively used to determine the fractal dimension of surface and volume fractals. Here, there is again the possibility of ambiguous interpretation of results.[3] For example, the slope of the straight line obtained by plotting ln(structure factor) vs ln(energy transfer) is normally 4. Any deviation from 4 is often identified with fractality. But polydispersity[4] in the size of the objects studied may also cause such deviation.

We suggest in this paper that quasielastic incoherent neutron scattering (QINS) from diffusing particles confined to a fractal space may exhibit certain characteristic features not observed for normally diffusing particles. Quasielastic incoherent neutron scattering or light scattering is an important tool for investigating diffusive motion in condensed media.[5]

Whereas coherent quasielastic scattering yields information about pair correlation functions and their time evolution, QINS effectively follows the diffusive motion of particles and gives information about the diffusion path and mobility. Particles diffusing within a fractal space are expected to occur in interesting systems such as protons in certain gel-type superionic conductors,[6] Ag^+ ions in percolating networks of AgI in AgI phosphate or borate glasses,[7,8] and in biological systems. In this paper we consider the case of superionic glasses.

QINS experiments have been reported for single crystals[9] and glassy superionic materials.[7] In single crystals the scattering depends on the direction and magnitude of the momentum transfer $\mathbf{k}$ of the neutron, but in glassy samples the scattering is isotropic. The line shape of the scattered intensity and the $\mathbf{k}$ dependence of the half-width of the scattering profile are distinctive features, and may serve as tests for different proposed theoretical models of ionic conduction.

The process of ionic conduction in superionic glasses is not yet well understood. In $(AgI)_x$-$(AgPO_3)_{1-x}$ and $(AgI)_x$-$(Ag_2O,B_2O_3)_{1-x}$ glasses a possible mechanism may be ion transport through clusters of the AgI component, which is known to be a good superionic conductor.

In this case an infinite cluster or percolation path through the AgI phase is necessary for conduction. This again gives rise to another interesting question. It has been shown that the infinite cluster at the percolation threshold exhibits a fractal structure,[10] and diffusion through a fractal shows anomalous behavior. This has been observed for percolation clusters also.

Normally one expects the QINS intensity vs frequency line shape to be a Lorentzian centered at $\omega=0$ and with a half-width proportional to k^2 for small k.[11] These relations have been derived assuming diffusion to be normal, i.e.,

$$\langle r^2 \rangle \sim t , \tag{1}$$

where $\langle r^2 \rangle$ is the mean square distance traversed by a diffusing particle in time t. The proportionality constant contains the diffusion coefficient D.

For diffusion in fractals, however, the diffusion is anomalous with

$$\langle r^2 \rangle \sim t^{2/d_w} \tag{2}$$

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where d_w is an exponent other than 2, and depends on the fractal dimension d_f of the medium and its connectivity, which may be characterized by the exponent d_s,[10] the spectral dimension. This has been suggested from scaling arguments[12] and demonstrated by simulation on deterministic[13] and random fractals like percolation clusters. d_w, d_s, and d_f are in general noninteger.

Our aim is to see how the QINS line shape is affected if the diffusion law is given by Eq. (2) instead of Eq. (1). We use values of the fractal exponents reported by different authors for percolation clusters in three-dimensions to calculate the QINS cross section. Here the fractional exponents do not permit analytical integration and the scattering cross section has to be calculated numerically. The line shape thus obtained is compared to the usual Lorentzian curve.

II. THEORY

A. The QINS cross section

The quantity measured in a scattering experiment is the differential scattering cross section, which describes the probability of an incident neutron or photon having a certain energy being scattered into a definite solid-angle element within a certain energy range.[11]

The scattering cross section is proportional to the dynamical structure factor, which consists of two parts—a coherent contribution due to interference between waves scattered from different nuclei, and an incoherent contribution due to scattering from waves originating from the same nucleus as it diffuses through the medium. Van Hove scattering laws are

$$S_{\mathrm{coh}}(\mathbf{k},\omega)=(2\pi)^{-1}\int \exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]G(\mathbf{r},t)d\mathbf{r}\,dt \quad (3)$$

for coherent scattering, and

$$S_{\mathrm{incoh}}(\mathbf{k},\omega)=(2\pi)^{-1}\int \exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]G_s(\mathbf{r},t)d\mathbf{r}\,dt \quad (4)$$

for incoherent scattering. $G_s(\mathbf{r},t)$ represents the probability of finding a nucleus at r at time t is the same nucleus were at $r=0$ at $t=0$. See Springer.[11]

B. Normal diffusion in Euclidean space

The function $G_s(\mathbf{r},t)$ is usually approximated by a Gaussian as follows:[11]

$$G_s(\mathbf{r},t)=[4\pi\gamma(t)]^{-3/2}\exp[-r^2/\gamma(t)] \ . \quad (5)$$

For normal diffusion $\gamma(t)$ is linear in t,

$$\gamma(t)=Dt \ , \quad (6)$$

D being the diffusion coefficient. This expression for $G_s(\mathbf{r},t)$ gives Eq. (1). The scattering law under these conditions is a Lorentzian profile:

$$S_{\mathrm{incoh}}(\mathbf{k},\omega)=\frac{k^2D/\pi}{\omega^2+(k^2D)^2} \ . \quad (7)$$

In the low-$\mathbf{k}$ limit the width of the quasielastic line at the half maximum is proportional to k^2.

C. Anomalous diffusion in fractals

For diffusion problems in Euclidean space, the function $G_s(\mathbf{r},t)$ is of Gaussian type. But this sample behavior can no longer be applied in fractal spaces. The form of the function $G_s(\mathbf{r},t)$ for percolation clusters and several fractal spaces has been studied by different authors.[14–17] All the proposed forms of $G_s(\mathbf{r},t)$ for fractals have the simple scaling form

$$G_s(\mathbf{r},t)\sim[V_s(t)]^{-1}F\left[\frac{r}{t^{1/d_w}}\right] , \quad (8)$$

where $V_s(t)$ is the volume accessible to the random walker in time t. Taking into account the scaling of the density of the fractal substrate, this becomes

$$G_s(\mathbf{r},t)\sim\frac{r^{d_f-d}}{t^{d_s/2}}F\left[\frac{r}{t^{1/d_w}}\right] . \quad (9)$$

d_f and d_s are the fractal and spectral dimensions, respectively, d is the embedding Euclidean dimension, and d_w is the diffusion exponent defined earlier in Eq. (2).

The exact form of the function $F(x)$, with x as the scaling variable ($r/t^{1/d_w}$), is controversial. Several authors have considered scaling forms of $F(x)$ using different approximations for some deterministic fractals and two-dimensional (2D) percolation clusters.

We have taken the form of $G_s(\mathbf{r},t)$ suggested by Guyer[16] as

$$G_s(\mathbf{r},t)\sim\frac{r^{d_f-d}}{t^{d_s/2}}\exp\left[-\left[\frac{r}{t^{1/d_w}}\right]^u\right] , \quad (10)$$

where

$$u\sim\frac{d_w}{d_w-1} \ . \quad (11)$$

The expression for $u\,[=d_w/(d_w-1)]$ is seen to be valid only for loopless structures. However, it can be approximated for aggregates with a small number of loops. Percolation clusters are usually found to have only a small number of loops[10] and, therefore, Eq. (10) is valid for percolation clusters with u taken approximately as $d_w/(d_w-1)$. The results obtained for 2D percolation clusters show good agreement with (10) where the calculated value of u from relation (11) is 1.53 and a fit to the numerical data gives a slightly higher value, 1.65 ∓ 0.1. For 3D percolation clusters, we have taken u to be 1.37 according to relation (11).

The Sierpinski gasket is an example of a fractal structure with loops. The numerical value of u for Sierpinski gasket comes out to be 1.9 ∓ 0.1 whereas the calculated value [from relation (11)] is 1.76. Numerical calculations have been performed on the Sierpinski gasket in different x regimes to test the form of the scaling variable x.[18] It has been found that in the $x\gg1$ regime, i.e., the asymptotic limit, the form of the scaling function agrees with the proposed form of Guyer.[18]

Our interest is to see how Eq. (10) is modified if $G_s(\mathbf{r},t)$ is given by Eq. (8) instead of by Eqs. (5) and (6). We calculate $S_{\text{incoh}}(\mathbf{k},\omega)$ with parameter values reported in standard literature,[9] for percolation clusters in three dimensions.

We have taken $d_f=2.51$, $d_w=3.68$, $d_s=1.328$, and $u=1.37$. With such values, the integral in Eq. (4) reduces to

$$S_{\text{incoh}}(\mathbf{k},\omega)=2\int_0^{\infty} dt \frac{\exp(-i\omega t)}{t^{d_s/2}} \times \int r^{d_f-d+2}\frac{\sin(kr)}{kr} \times \exp[-(r/t^{1/d_w})^u]dr \,, \qquad (12)$$

which cannot be calculated analytically any further. Even for very small values of k, the asymptotic behavior cannot be obtained because of the r integral ranging from zero to infinity. The calculation has been done numerically for different k values and compared with the Lorentzian. Preliminary calculations have been reported by Tarafdar and Ballabh.[19] The double Fourier integral has been performed by the Gaussian quadrature method and it has been found that the results are correct up to three decimal places.

The QINS line shape is found to deviate significantly from the Lorentzian. Further, the width at half maximum of the profile is independent of k. $S(\mathbf{k},0)$, the peak intensity varies, with k according to a power law. The possible implications of these results are discussed in the next section.

III. RESULTS AND DISCUSSION

Figure 1 shows the quasielastic scattering line shape calculated for anomalous diffusion and compares it with the Lorentzian. It is seen that the two curves are markedly different in shape, indicting that quasielastic scattering may be used to identify anomalous diffusion and hence the presence of a fractal diffusing space for charge carriers in a superionic conductor. A striking feature is the presence of weaker secondary maxima. The line shape has an oscillatory nature, unlike the Lorentzian.

Quasielastic incoherent scattering has been observed in several superionic conductors.[7-9] In $SrCl_2$ single crystals[9] the diffusing space is obviously Euclidean. In AgI phosphase glasses, however, the diffusing path is probably through the percolating network consisting of AgI clusters. At AgI concentrations close to 0.3, i.e., the percolation threshold, the quasielastic line shape is expected to be similar to the calculated curve in Fig. 1.

It can be seen qualitatively that the experimental line shape given by Rodriguez, Benassi, and Fontana[7] agrees better with our calculated curve than the Lorentzian fit, which is actually a superposition of two Lorentzians. The justification for using two Lorentzians is not clear. Moreover, the data points do appear to show an oscillatory nature, and the presence of secondary maxima cannot be ruled out. Another interesting point is that the data showing variation of half-width with the AgI concentration[7] appear to have a sudden change near the percolation threshold around x close to 0.3.

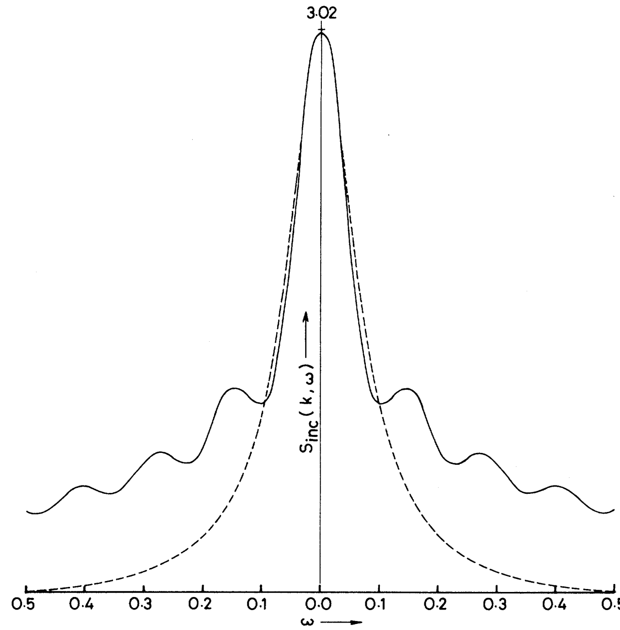

FIG. 1. Plot of scattering intensity S_{incoh} vs ω. Solid line shows S_{incoh} calculated from present model and broken line the closest Lorentzian. Units for ω and S_{incoh} are arbitrary.

A marked oscillating nature may also be noticed in the experimental results reported by Fontana *et al.*[8] Figures 8 and 9 of that paper show plots of $I_R/g(\omega)$ vs frequency shift. The small-frequency-shift region is identified as the quasielastic region. The distribution of points here appears to be systematically oscillating rather than randomly scattered towards the large-k side. The authors focused their attention on the fracton region and have not discussed this aspect, but it seems that the fractal nature has also left its signature in this low-k region. The secondary maxima probably represent excitations caused by long-range correlations in the fractal.

The width of the central peak being independent of k seems surprising since in normal lattices there is a marked k dependence, and in the small-k limit, the width at half maximum

$$\Gamma \propto k^2 \,. \qquad (13)$$

In cases where there is deviation from the normal diffusion law,[20] e.g., polymers, there is a different k dependence. It may be seen, however, that for fractals this result is not unexpected, because, being self-similar, i.e., invariant on all length scales, fractals actually do not have a small-k (long-wavelength) limit. A true fractal never looks like a continuum, no matter how large the wavelength of the probing radiation; on the other hand, a lattice which has an intrinsic length scale looks like a continuum for radiation with $k\neq 0$ and this gives rise to the long-wave behavior. This basic difference of the "normal" and fractal structures is incorporated in the present calculation, through $G_s(\mathbf{r},t)$ in (10). A real glass, however, will not be a fractal except within a certain range of length scales. So one should look for this peculiarity in the range of k values appropriate to such scales. We have not come across experimental data on the k dependence of QINS in superionic glasses or other systems which may exhibit such behavior, so we cannot check this point.

A recent book[5] on QINS gives a discussion of scattering in bound spaces, but there is no direct reference to the situation in fractal spaces. However, the experimental data on water-soaked polymer membranes[5] (p. 373) show a regime where the half width at half maximum (HWHM) remains constant with variation of k. It may be possible to interpret those results by a fractal model.

$\ln S(k,0)$ plotted against $\ln(k)$ is shown in Fig. 2. The points fall almost exactly on a straight line with slope around 2.6. Within the limits of error, this appears to imply a relation

$$S(k,0) \sim (1/d^{d_f}) \tag{14}$$

as reported for small-angle scattering in fractals,[2] since the Hausdorff dimension d_f has been taken as 2.51 in the present paper.

More experimental data on QINS in systems suggested to have a fractal nature are required to verify the predictions of the present paper. In view of the ambiguity usually present in identifying a real system as fractal, such experimental studies covering different aspects of fractality are badly needed. Direct independent measurement of the fractal dimension d_f, spectral dimension d_s, and random-walk exponent d_w for the same fractal has not been performed yet to our knowledge. This would also serve as a test of the validity of the relations connecting different fractal exponents suggested by Rammal and Toulouse.[21]

Further work on superionic glassy systems and biological systems such as liposomes would be useful.[22] Proton conductors are also promising candidates for QINS studies, due to the large incoherent scattering cross section of

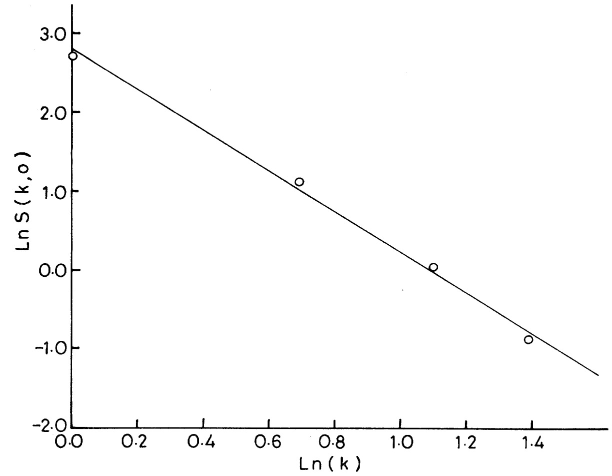

FIG. 2. Plot of $\ln[S(k,0)]$ vs $\ln(k)$.

protons. This has been discussed by Lechner.[23] Studies on gel-type proton conductors with large surface area[6] may also reveal non-Lorentzian line shapes.

Another superionic material where QINS may be tried is $SrCl_2$-alumina composite. Here also ionic conduction probably takes place through a percolation network, i.e., a fractal space, and the mobile Cl^- ion has a large incoherent scattering cross section.

In conclusion, QINS in fractal spaces with anomalous diffusion promises to show interesting new features, and further experimental and theoretical work in this field should be rewarding.

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