# Diffusivity and pore distribution in fractal and random media

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The diffusion of a gas particle in a porous medium (fractal or random) is studied. Diffusivity and pore chord distribution are computed for different gas particle sizes and different densities of the porous media. This calculation allows us to estimate the critical density where the gas does not percolate from one side to the other side of the porous medium. [S1063-651X(99)10903-6]

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## I. INTRODUCTION

Disordered porous solids play an important role in industrial processes such as separation science, heterogeneous catalysis, oil recovery, glass, and ceramic processing [10]. The confinement and the geometrical disorder of these systems strongly influence the dynamic or thermodynamic processes which can take place inside the pore network.

Several studies have been made on the diffusion of finite size particles in porous media [1–4]. These studies were mainly focused on diffusion in random media. Works on long-range correlated media, as, for example, fractal media, can be found in [5–7].

To study the diffusivity in random or fractal media, one may use different methods such as Monte Carlo simulations, analytical or numerical hydrodynamical approach, and Brownian motion simulation techniques.

We shall study here the influence of the size of the gas diffusing particle on the diffusion constant. The gas particle will be diffusing either in a random medium or in a fractal medium.

Another interesting feature which is related to the diffusion problem is the pore chord distribution [8,9]. A pore chord distribution is a segment belonging to a pore and having both ends on the interface pore-solid medium. It can be considered as a linear path, which is correlated to different points of the interface. The pore chord distribution is a direct characterization of the pore distribution as a function of the pore size and may give indications on the fractal structure of the solid medium in which the diffusion takes place. We shall focus on the pore chord distribution in fractal and random media, and compare these two media in that respect.

A third point that we shall deal with here is the numerical calculation of the percolation concentration for the diffusion of finite size particles. Up to now, no exact calculation of the percolation threshold of random (or fractal) media has been made. We propose here a numerical method which allows us to compute this percolation threshold for random packings of nonoverlapping spheres.

## II. THEORY AND NUMERICAL PROCEDURE

We used the same numerical procedure as in Ref. [5]. The fractal medium is built using a three-dimensional off-lattice diffusion-limited cluster-cluster aggregation method (DLCA method) [11,12]. The numerical simulation of the gas motion proceeds as follows: initially a sphere is released at random inside the pores under the condition that it should not overlap with any other sphere. Then the sphere is allowed to follow a straight line motion in a chosen random direction (uniformly distributed in space) until it collides with another sphere of the solid medium (fractal or random). Immediately after collision, a new random direction is selected (in a half-space) according to the so-called Knudsen cosine law [13,14]. After a large number of collisions, and using periodic boundary conditions, one calculates the end-to-end square displacement $l^2$ as well as the total length of the trajectory $\Lambda$. This allows us to calculate the diffusion constant $D$:

$$D=\frac{1}{6}v\frac{l^2}{\Lambda}, \tag{1}$$

where $v$ $(=\sqrt{8kT/\pi m})$ is the mean molecular velocity of the gas particle of mass $m$ at temperature $T$. The influence of the size of the gas particle is computed by simply increasing the numerical gas particle radius.

Recalling Ref. [5] , a simple calculation gives a diffusion constant for packings of nonoverlapping spheres:

$$D\propto(c_{\mathrm{crit}}-c)^{1/3}/c, \tag{2}$$

where $c$ is the density of the packing and $c_{\mathrm{crit}}$ is the percolation concentration for a given size of gas particle (i.e., the concentration for which the gas particle can no longer diffuse from one side of the simulation box to the other side).

An adequate plotting allows us, by using formula (2), to estimate the critical concentration $c_{\mathrm{crit}}$ for packing of nonoverlapping spheres and a zero gas particle radius.

For packings of overlapping spheres, the corresponding formula is slightly different (see Ref. [5]):

$$D\propto\frac{(c_{\mathrm{crit}}-c)^{1/3}}{c^{1/3}}\frac{d\ln c}{ds}, \tag{3}$$

where $s$ gives the solid medium sphere radius by $R=R_0(1+s)$, where $R_0$ is the sphere radius for the corresponding packing of nonoverlapping spheres (assuming that all the overlapping spheres have the same radius).

Another interesting theoretical point is the pore chord distribution. For details, see Ref. [9]. We shall give here a brief

 

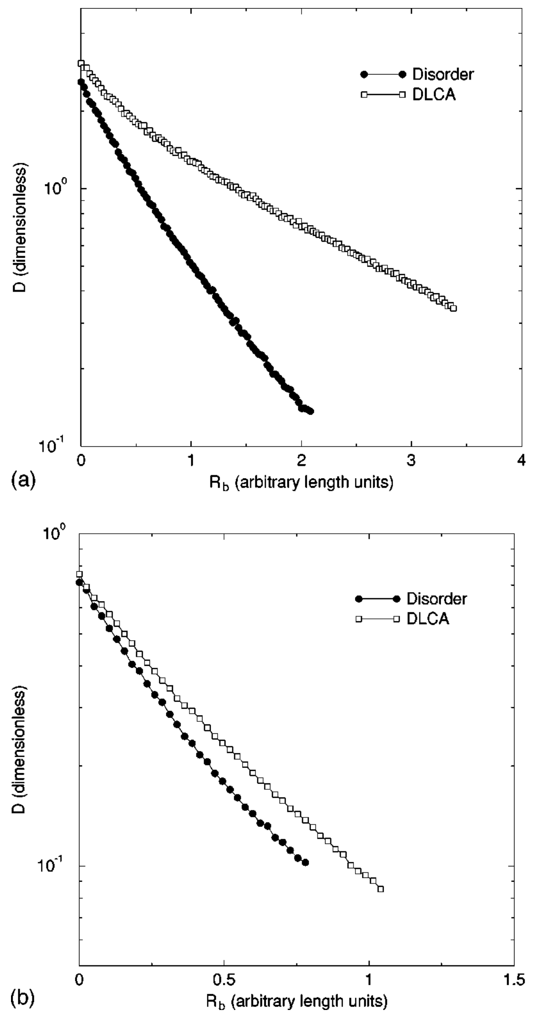


FIG. 1. (a) Linear logarithmic plot of the diffusivity as a function of the gas particle radius $R_b$ for random media (black circles) and fractal media (squares). The density of the media is $c=0.05$. (b) Linear logarithmic plot of the diffusivity as a function of the gas particle radius $R_b$ for random media (black circles) and fractal media (squares). The density of the media is $c=0.2$.

summary of this paper: the chord size distribution ''in number'' is related to the conditional probability of having a chord size (a segment linking to spheres surfaces) between $r$ and $r+dr$. If the packing has a fractal distribution of mass, the pore chord distribution scales as

$$f(R) \propto \frac{1}{R^{D-1}}, \tag{4}$$

where $R$ is a given pore chord size and $D$ is the fractal dimension of the sphere packing.

### III. NUMERICAL RESULTS

In Fig. 1(a), we plotted the diffusivity (diffusion constant $D$) as a function of the gas particle radius $R_b$ for a disordered medium and for a fractal medium built with the DLCA method. The graph is of linear logarithmic type. As we can see, the curve for the disordered medium is almost linear for this type of plotting. For the fractal (DLCA) case, there is a larger curvature near $R_b=0$, then the curve becomes linear,

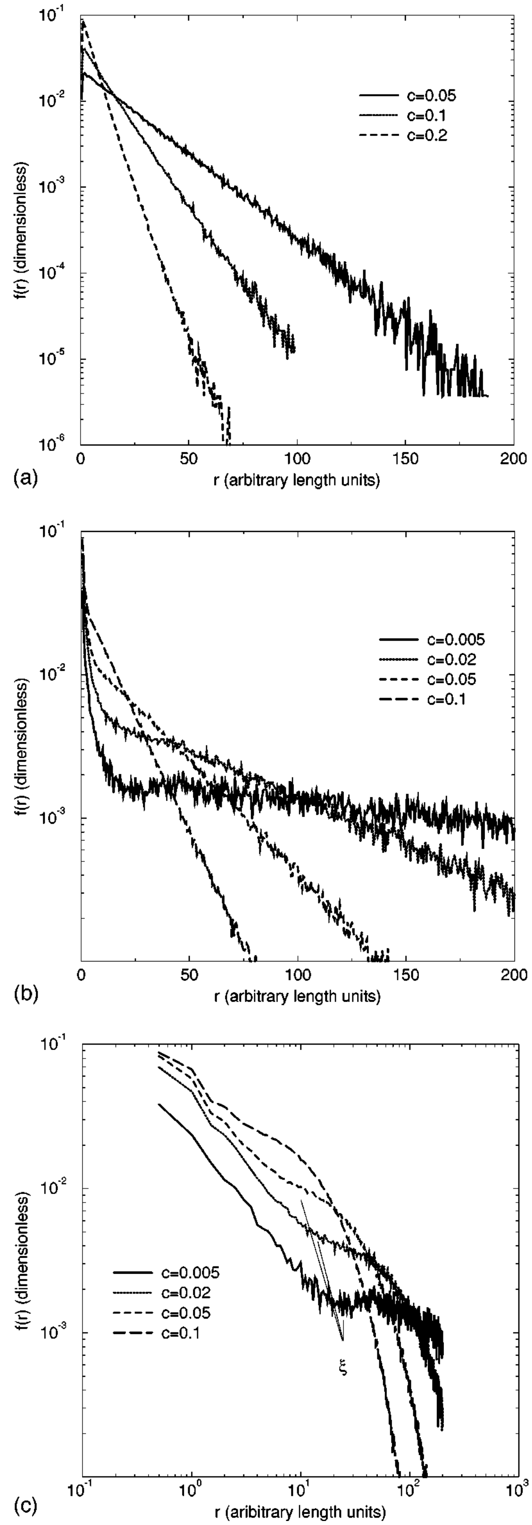


FIG. 2. (a) Linear logarithmic plot of the pore chord distribution for random media. Three different densities of the media have been used: $c=0.05$ (black line), $c=0.1$ (dotted line), and $c=0.2$ (dashed line). (b) Linear logarithmic plot of the pore chord distribution for fractal media. Four different densities of the media have been used: $c=0.005$ (black line), $c=0.02$ (dotted line), $c=0.05$ (dashed line), and $c=0.1$ (long dashed line). (c) Log-log plot of the pore chord distribution for fractal media. Four different densities of the media have been used: $c=0.005$ (black line), $c=0.02$ (dotted line), $c=0.05$ (dashed line), and $c=0.1$ (long dashed line).

and the diffusivity becomes larger than that of the random medium. This is a consequence of the fractal character of the medium. We can see that in absolute, the diffusivity for the fractal medium is higher than for the random medium: in the fractal medium, the mean-square displacement of the gas particle diverges until it reaches an upper limit which is proportional to the fractal domain size. For this density of fractal medium ($c = 0.05$), the fractal domain is large enough to see this divergence. In fact, the diffusing gas particle has its path which is essentially located in large pores. The probability for one gas particle to begin its motion in a small pore is very small, so the contribution to the diffusivity of the small pores is negligible compared with the contribution of the gas particle path in large pores.

As a matter of fact, in Fig. 1(b), the difference between diffusivity in random (circles) and fractal (squares) media is smaller than in Fig. 1(a). The density is higher ($c = 0.1$) and so the fractal domain is smaller and hence the fractal character of the medium has a small influence on the diffusivity: diffusivities for random and fractal media do not differ very much for this density.

In Fig. 2(a), we plotted the pore chord distribution for different densities of random media. In a linear-logarithmic plot, one may see that the curves are linear. This is characteristic of random media: the behavior of the pore chord distribution is exponential.

On the contrary, for fractal (DLCA) media, in a linear-logarithmic plot, the pore chord distribution has two regimes: the first regime, for pores radii near 0, shows a curve with a nonexponential behavior; then in the second regime, the curves recover their exponential behavior (they are linear in a linear-logarithmic plot). This may be interpreted as follows: the pore chord distribution is influenced by the fractal character of the medium. In the first regime, the probability to have a given pore size is directly related to the fractal structure of the matter.

The same data were plotted in Fig. 2(c) but in a log-log graph. The first regime is located between 0.5 and $10^1$. The second regime (where fractal correlations do not have any further effects) appears after $10^1$. This graph allows us to estimate the upper limit of the fractal domain $\xi$ which is the limit of the power-law behavior of the pore chord distribution. Following Fig. 2(c), the fractal domain upper limit runs from $10^1$ to $2\times10^1$. But, this is a graphical estimation of $\xi$ and the uncertainty on these values is about 1.

In Fig. 3(a), we plotted the diffusivity for a zero radius particle as a function of the density of the medium (fractal or random). We see that, in a log-log plot, the two curves do not differ much.

Figure 3(b) shows the cube of the diffusivity multiplied by the density as a function of the density. Using formula (2), this plot allows us to estimate the percolation density (for which the gas particle no longer percolates). For random media, the critical density is about 0.72 and for fractal structures this density becomes close to 0.6. This extrapolation is valid for packing of nonoverlapping spheres.

## IV. DISCUSSION

The diffusivity of a zero size particle in a random medium is different from the diffusivity in a fractal medium. According to Levitz [15], in fractal media the mean-square displacement, for fractal dimensions $1 < D < 2$, runs as

$$\langle R^2 \rangle \propto t^{-2D+6}, \tag{5}$$

where $t$ is the time (equivalent to the total length of the gas particle trajectory). This mean-square displacement has an upper limit for finite fractals which is proportional to the size of the fractal domain. So although the mean-square displacement diverges, the diffusion constant is finite. As a matter of fact, for larger fractal domains, the diffusion constant will be larger. That explains the discrepancy between the diffusivity in random and fractal media and explains that the diffusivity is larger for lower densities of fractal media.

The pore chord distribution is directly related to the mean free path of the gas particle. Indeed, as the gas particle has a ballistic motion between two collisions with the porous medium, each free path is a pore chord, i.e., the distance between two points on the surface of the porous medium. It is interesting to see that for random media, the pore chord distribution has an exponential behavior, whatever the pore

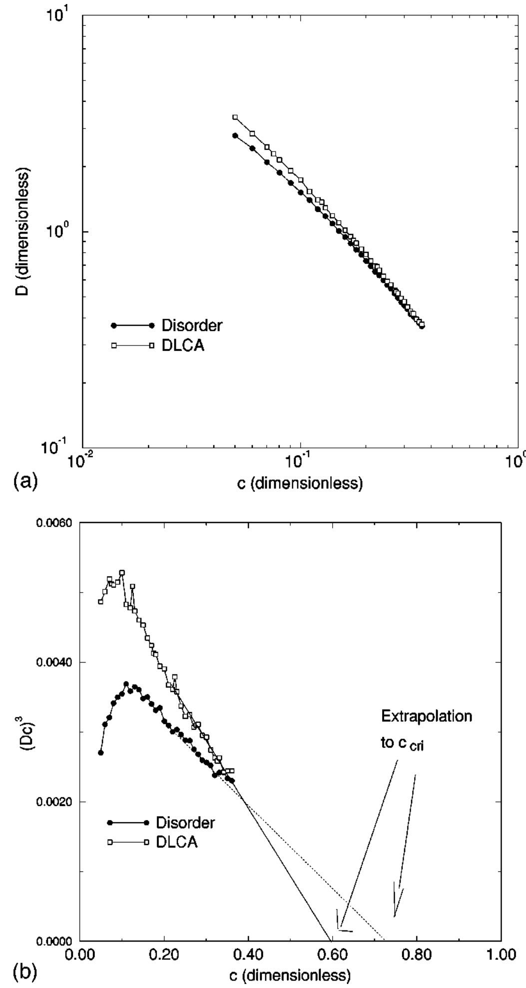


FIG. 3. (a) Log-log plot of $Dc$ (in dimensionless units) as a function of the density of the porous media, for random media (black circles) and fractal media (squares). (b) Linear plot of $(Dc)^3$ versus $c$, where $D$ is the diffusivity and $c$ is the density of the porous medium, for random media (black circles) and fractal media (squares). The extrapolation of these two curves allows us to estimate the percolation densities $c_{\mathrm{crit}}$.

chord size is. This is a characteristic feature of the random distribution of pore sizes in the case of random porous media: the pore sizes have no correlation. So the diffusivity in random media is dominated by the smallest pore sizes: the gas particle has a probability which increases exponentially, when the sizes of the pores decrease, to remain in a pore. In the case of fractal media, the pore chord distribution has a power-law behavior for the smallest pores, and then for larger pores the pore chord distribution becomes exponential. This is the effect of the fractal correlations of matter in fractal media, which influences the distribution of pore sizes. So, the mean-square displacement diverges until it reaches the limit of the fractal domain. If the fractal domain is large, the gas particle may have a hyperdiffusive behavior: the gas particle may stay a very long time in a small pore and then suddenly reach a large pore . This is a Levy flight behavior. The large free path influences the mean-square displacement but not the mean free path as they are very rare. If the fractal domain were not limited, it would not be possible to compute the diffusivity, as the mean-square displacement would diverge to infinity.

Another interesting point that we studied here is the critical density of the porous medium, for which the gas particle can no longer diffuse from one side to the other side of the sample. It is evident that this critical density depends on the size of the gas particle and on the geometrical repartition of matter in the porous medium. We found different values of this critical density for a zero size particle. In this case [Fig. 3(b)], the critical density may be related to the percolation density: as the gas particle is of zero size, the critical density corresponds to the case where the pores have no more connections. So the critical density $c_{\rm crit}$ may be related to the site percolation critical density $c_{\rm site}$ by $c_{\rm crit}=1-c_{\rm site}$.

## V. CONCLUSION

We computed here the diffusivity of a gas particle through porous media, either fractal media or random media. The gas particle diffusivity is studied as a function of the gas particle size and of the porous media density. To understand the behavior of the diffusivity, we computed the pore chord distribution, i.e., the probability to have a given size of pores. In fractal media, this probability has a power-law behavior and the diffusivity diverges: this is a consequence of the fractal pore size distribution. In random media, the pore chord distribution decreases exponentially, so the mean-square displacement evolves proportionally to the total length of the trajectory which allows us to compute the diffusivity. Finally, the critical density related to the site percolation density is numerically computed by the mean of the diffusivity.

It would be interesting now to compute the diffusivity as a function of the gas particle size and the porous medium density for different fractal dimension. A question which arises for future study is as follows: is the site percolation density dependent on the fractal dimension and does ‘‘diffusivity’’ mean anything for large fractal domains?

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