Biological Engineering Conference - CHEMPOR 2008
Braga, Portugal, September 4-6, 2008
E.C. Ferreira and M. Mota (Eds.)

Hindered Motion in Highly Porous Media: Steric and Fractal Approaches

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Keywords: Hindered diffusion, Porous media, Fractal, Simulation
Topic: Advancing the chemical and biological engineering fundamentals.

Abstract

Two-dimensional simulation of porous media using a pore fractal dimension D was performed. Obtained results can be outlined as follows: 1). Starting from large pores with aspect ratio of micro-particle size to pore size λ > 0.001, molecules (or test object) recognise the pore volume as a partially restricted space with reduced fractal dimension. 2). The restriction effect on a molecule depends on pore topology (in the present case on the type of packing). 3). Dramatic reduction of D is observed when λ overcomes 0.01 and approaches λ ~ 0.1 in a 2-D approach, meaning that the test object recognises the pore as one dimensional rather than a 2-D space; in turn, a 3-D system will be recognised by the the test object as a 2-D system. 4). Concerning the hydrodynamic chromatography (HDC) the simulation explains why micro-objects become significantly retarded even at λ ~ 0.01, that is, even when the ratio between the Stokes-Einstein diameter of the diffusing micro-object to the equivalent pore diameter is very small. The developed approach confirms that even for micro-object with a very simple geometry (a square test box) a molecule might be much more sensitive to pore topology than what could be expected by a steric effect. It is possible to expect a more pronounced effect for asymmetric micro-objects in tortuous channels. These results show that the problem of molecular sensitivity towards pore topology may be understood using fractal analysis. Further work will apply this fractal approach to diffusivity behaviour in gel-like and fibre-like or foam structures.

1. Introduction

The quest for higher resolution in macromolecules bio-separation, nano-particles, viruses and micro-organisms, together with the requirement to keep their full bioactivity by preserving their shape and conformation is calling for new approaches in the bio-separation field. A hydrodynamic theory developed for the diffusion and convection of micro-objects in porous media for the case of hindered motion was presented in a previous work of Mota et al. (2006) and can be briefly summarised as follows.

The pore topology plays an important role in the separation of micro-particles of different shapes when the aspect ratio (micro-particle size)/(pore size) approaches λ = 0.1. The complexity of the observed retardation phenomenon needs further investigation to clarify the interaction particle-pore topology mechanism. The obtained results may open interesting applications for bio-separation, for deep bed filtration, and to understand the motion of micro-objects (for instance viruses and nano-particles) in porous media.

2. Hindered diffusion

The effective diffusion coefficient D_e of a solute in a channel is composed of two correction functions, $F_1(\lambda)$ and $F_2(\lambda)$: $D_e = D_0 F_1(\lambda) F_2(\lambda)$, where D_0 is the bulk diffusion coefficient and λ is the ratio of Stokes-Einstein diameter of the diffusing

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micro-object d_m to the equivalent pore diameter d_{por}, $\lambda = d_m / d_{por}$. The parameter $F_1(\lambda)$ is the steric partition coefficient, which is defined as the cross-sectional area of the pore available to the solute molecule divided by the total cross-sectional area of the pore

$$F_1(\lambda) = (1-\lambda)^2 \tag{1}$$

The correction factor $F_2(\lambda)$ accounts for the effect of the pore wall on the solvent properties (an increase in the local solvent viscosity near the pore wall) and is often represented by a polynomial series, as displayed in equation (2), or by an exponential function, as displayed in (3). Other model functions are particular cases of (2) or (3)

$$D_e / D_0 = (1-\lambda)^2\left[1 - 2.1044\lambda + 2.089\lambda^3 - 0.948\lambda^5\right],\ \lambda \le 0.5 \tag{2}$$

$$D_e / D_0 = (1 - 1.83\lambda + 4.18\lambda^2)\exp(-6.52\lambda) \tag{3}$$

Numerous experimental results show that hindered diffusion and convection depend not only on equivalent micro-object and pore sizes, but on the pore topology as well, (Mota et al., 2006). Havsteen (1993) analysed non-classical flow through narrow-pored membranes and concluded that when the passages through the membrane become small enough in comparison with the size of the percolating molecules, fractal properties of the pore must be accounted for. Giona et al. (1996) admit that the topology complexity of a fractal pore network modifies the scaling properties of diffusion.

Using a 2-D model, when pore size is significantly larger than a molecule, fractal dimension tends to the topological value of 2. When the pore scale gets close to the size of a molecule, the fractal values become close to the topological dimension of unity. For better understanding transport phenomena in porous materials it is interesting to know how a molecule will behave in the porous space geometry between the aforementioned boundaries.

To consolidate the experimental observations, a two-dimension porous media simulation was made with a disc packing.

3. Simulation conditions

Pore area fractal analysis was performed by a test-box counting method

$$\log\left[N(r)\right] = \log(k) - D_{pa}\log(r) \tag{4}$$

where D_{pa} is the porous area fractal dimension; $N(r)$ is the number of boxes of side length r needed to cover a porous medium image. The test-box simulates a compact micro-object inside the pore space formed by discs packing.

The fractal dimension was measured by means of the commercial software *Fractal Vision* 2.5, Oliver (1992). This software was successfully applied to quantify the surface roughness of flocs and granules and gave a quite reasonable estimation of the fractal dimension, as reported by Bellouti et al. (1997). The *Fractal Vision* algorithm allows determining the fractal dimension of an image tested by three types of box size r = 2, 4 and 6 pixels, Oliver (1992). The molecule size in simulation was assumed to be equal to the test box size r.

Image in pixel's representation has rough bounds with a minimal size resolution of 1 pixel. This roughness simulation imitates the rough channel surface. The ratio of roughness scale to the discs size, that builds the porous medium skeleton, will be variable. The ratio increases when disc size decreases. Such behaviour means that, for a fixed molecule size, decreasing the porous medium scale results in a more active role of roughness. This fact does not contradict known reports. For instance, Douglas, (1989) during simulation of fractal surface adsorption observed a great probability of polymer-surface interaction with increasing roughness.

All images of porous media are considered as cross-sections that are perpendicular to the direction of the molecule diffusion and the measured parameter was the fractal dimension of pore area D_{pa}. The following two-dimensional models of porous media have been used: 1) binary and ternary mixtures of different size and fraction of discs; 2) regular uniform disc square and hexagonal packings.

4. Results and discussion

4.1. Binary and ternary packings

Binary and ternary mixtures of different size and fraction content of discs were built by the algorithm described by Mota et al. (1999). The mixture model was used in the cited research for investigation of porous media geometry: porosity, tortuosity, etc. Procedure of the binary porous medium building was based on randomly packing and compacting of discs in order to obtain high-density packing. The ternary mixture model is built by filling the void space of a binary mixture with smaller discs. In simulation the following model of porous media were used: binary packing of discs with disc size ratio (1) : (1.9), (1) : (3.8), and (1) : (15.7); ternary packing, obtained from binary (1) : (1.9) and (1) : (3.8) packings, disc size ratio (1) : (4.5) : (8.6) and (1) : (3.36) : (12.8).

Fractal dimension of pores cross-section area D_{pa} is shown in Fig. 1 for two types of ternary (data sets 1 and 2) and three types of binary (data sets 3 – 5) systems as a function of fraction of large disc (x_D) in the packing. Discs size ratio is shown in Fig. 1 in brackets. Test disc boundary roughness was 1 pixel.

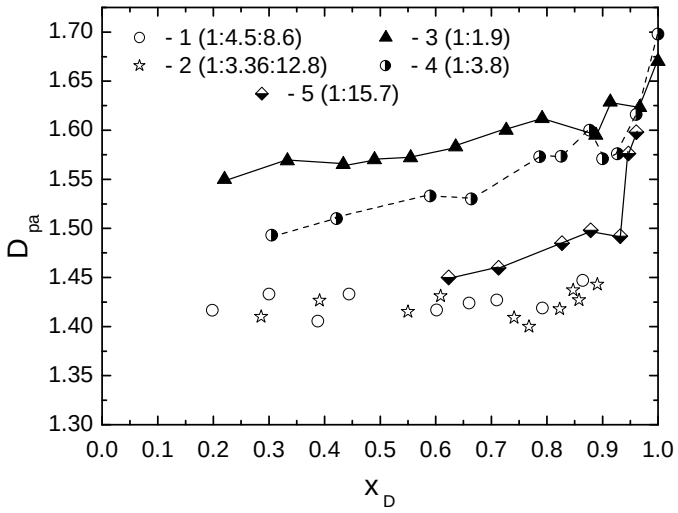

Figure 1. Fractal dimension of the porous area, D_{pa}, vs. fraction of largest discs in the mixture, x_D.

In binary packing, at the same fractional content x_D, increasing discs size ratio significantly reduced the fractal dimension that also depends on the large particle fraction in the mixture, x_D. The most dramatic D_{pa} decrease in mixtures with minimum porosity, occurs for x_D ~ 0.85 – 0.9 (Mota et al., 1999). Ternary mixtures built by filling the appropriate binary mixture free area by smallest discs have lower D_{pa} but are less sensitive to x_D.

For all binary mixtures the fraction of smallest discs which was possible to insert in free space, to get the ternary packing, was less than 10%. This observation leads to the conclusion that even a small amount of fine particles present in the binary packing can significantly affect on macromolecule diffusion because of the change in pores network topology.

Decreasing D_{pa} in binary packings for x_D below 0.8 is related with pore size

distribution when smallest pores have greater impact of the fractal dimension (Mota et al., 2004).

Concerning application to hydrodynamic (HDC) and slalom chromatography, we may assume that the process resolution may be improved by transition from monosize to the binary packing, at the same time saving the number of small size particles, usually more expensive. Binary packing is a well controlled system and the molecule's sensitivity can be controlled by particle fraction content and size ratio.

4.2. Fractality and diffusivity (fractal and steric approach)

To evaluate fractal and diffusive behaviour of porous media regular uniform square and hexagonal disc packings were investigated. The measured parameter was D_{pa} at different disc size versus the aspect ratio r/d_{por}: the ratio between the test-box size (r) and the equivalent pore size was determined based on disc size.

To compare the measured 2-D fractal dimension and 3-D diffusivity D_e/D_0 models (1-3), a re-normalisation procedure was performed based on the assumption that the equivalent pore diameter is $d_{por} = (2/3)[\varepsilon/(1-\varepsilon)]d$, where d is the sphere diameter; ε is the sphere packing porosity, ε = 0.476 for cube packing and 0.26 for hexagonal packing. Hence, the equivalent pore diameter is for cube packing $d_{por} \approx 0.6d$ and for hexagonal packing $d_{por} \approx 0.234d$, consequently, for other packing structures $d_{por} \approx a \cdot d$, a < 1, where d is the diameter of sphere equal to the diameter of disc. Finally, normalised pore size becomes $\lambda = d_m/d_{por} \sim r/d_{por} = r/(a \cdot d)$. Obtained results are shown in Figure 2.

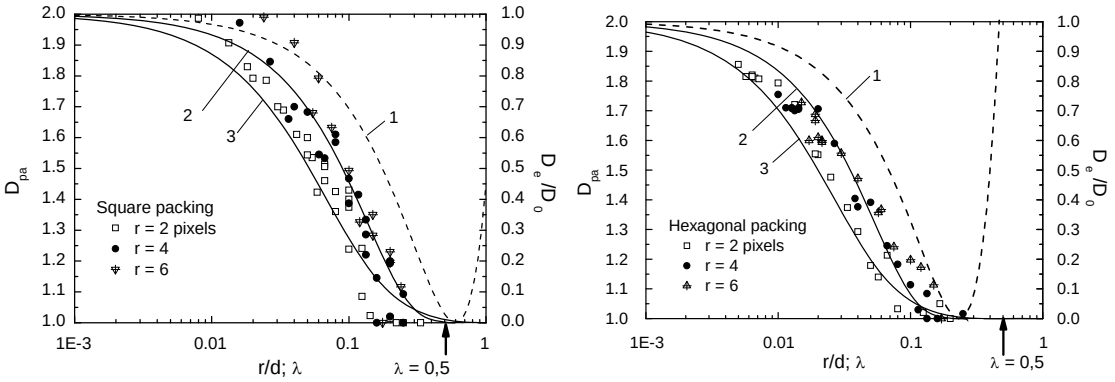

Figure 2. Dependence of D_{pa} on r/d and diffusivity D_e/D_0 on λ for square packing (a) and hexagonal packing (b) of uniform discs. 1 – Equation (1); 2 – Equation (2); and 3 – Equation (3).

The most important simulation result is the following: the range of molecule's "sensitivity" to the pore network cross-section area coincides to the hindered diffusion range. The main measured values of D_{pa} occupy an area between curve 1, equation (1) for steric partition coefficient, (cylindrical pore and spherical molecule) and curve 3, equation (3) for hindered diffusion of a macromolecule, whereas Renkin equation (2) is close to the scattering zone of the determined fractal dimension.

Concerning three dimension porous media, obtained results can be treated as follows: 1). Starting from large pores with λ > 0.001, molecules recognise the pore volume as a partially restricted space with reduced fractal dimension. 2). The restriction effect on a molecule depends on the pore topology (in present case on the type of packing). 3). Dramatic reduction of D_{pa} is observed when λ overcomes values around 0.01 and

approaches λ ~ 0.1 in 2-D approach meaning that the test object recognises the pore as one dimensional rather than a 2-D space; in a 3-D system the test object will recognise the pore with a behaviour closer to a 2-D system. 4). Concerning the hydrodynamic chromatography (Mota et al., 2006) the simulation explains why micro-objects become significantly retarded even at λ ~ 0.01, that is, even when the ratio between the Stokes-Einstein diameter of the diffusing micro-object d_s to the equivalent pore diameter is very low.

The developed approach confirms the fact that even for simple micro-object geometry (= test box) a molecule might be much more sensitive to pore topology than the predicted by the steric effect. It is possible to expect an even more pronounced effect for asymmetric micro-objects in tortuous channels, for example, branched and long macromolecules.

These results show that the problem of molecular sensitivity to pore topology may be satisfactorily solved using fractal analysis. Further work will apply this kind of approach to molecular diffusion inside gel-like, fibre-like or foam structures.

4.3. Molecule – pore size scale estimation

Based on fractal analysis let us estimate the pore diameter and disc (particle) size of uniform hexagonal packing model and the Tyn and Gusek (1990) list of protein sizes, assuming also that the test molecular size is equal to the protein size.

Calculations will be made 1) for hexagonal uniform sphere packing at two cases, namely, when test object recognises pore cross-section area with two fractal dimensions D_{pa} = 1.5 and 1.77.

Noting that $\lambda = r/(a \cdot d)$, for a hexagonal uniform sphere packing when D_{pa} ~ 1.5, the ratio $r/(0.234d)$ is around 0.03, and for D_{pa} ~ 1.3, $r/(0.234d)$ ~ 0.059, therefore, $d = r/(0.234\lambda)$. Assuming that twice the molecular gyration radius r_g is equal to the test box size ($r = 2r_g$), for the above defined D_{pa} we have the particle diameter $d = 2r_g/0.03/0.234$ or $d = 2r_g/0.059/0.234$. Obtained results are given in Table 1.

Table 1

Estimated packing particle size d for hexagonal uniform sphere packing recognised by test-box molecule as fractal medium with fractal dimension D_{pa} = 1.3 and 1.5.

Protein	Molecular weight	r_g, nm	D_{pa} = 1.5		D_{pa} = 1.3	
			d, μm	d_{por}, μm	d, μm	d_{por}, μm
Myoglobin	17,500	1.63	0.46	0.11	0.24	0.055
Ovalbumin	44,000	2.03	0.56	0.14	0.29	0.069
Catalase	225,000	3.98	1.13	0.27	0.58	0.13
Fibrinogen	340,000	14.2	4.05	0.95	2.06	0.48
Collagen	345,000	87.0	24.8	5.8	12.6	2.95
Myosin	493,000	46.8	13.3	3.12	6.78	1.59
DNA	4,000,000	117.0	33.3	7.8	16.9	3.97

Obtained data in Table 1 show that for a spherical particle we may expect a system's molecule-porous medium fractal behaviour in the submicron and micron range close to chromatographic column and micro-column packings for macromolecules such as fibrinogen. Moreover, the obtained particle size falls in the range of HDC and slalom chromatography modes (Hirabayashi and Kasai, 1996). Nevertheless, for proteins such as myoglobin, or ovalbumin, the determined particle/pore size is smaller and locates in nano-scale where data on chromatography are still scarce.

The carried out analysis considers the molecule as a square (2-D), but real

macromolecules are shaped, therefore, such type of macromolecules would be sensitive to pore topology even for r/d_{por} << 0.01 if the pore channel is rough and tortuous.

The drawback to porous media model analysis by the rectangular test box (molecule) is that such approach cannot be considered as a pure fractal analysis because of spatial scales dependence. Nevertheless, it seems interesting to get some “pseudo-fractal” dimension measurements for investigation of linear macromolecule interaction with porous media channel topology.

5. Conclusion

Images of 2-D porous media cross-section area generated on the simplest level of rough disc were analysed by test count method. The range of molecule’s sensitivity to the pore network cross-section area includes the range where hindered diffusion is observed. Renkin equation for hindered diffusivity is close to centreline of fractal dimension measured values.

The results confirm the idea that hindered diffusion effect may be described in fractality terms when pore wall is rough. It is possible to expect a more pronounced effect for asymmetric macromolecules in tortuous channel which can be subject of further investigation.

It was shown that hindered diffusion might be partially described in fractal dimension terms for porous media. Estimation based on bio-molecules size shows that the calculated by D_{pa} particle size is in the submicron and micron ranges close to chromatographic column packings.

It can be concluded that the problem of molecule sensitivity to the pore topology may be satisfactorily solved using fractal features but future work must validate obtained results. Other important point is to study the molecule sensitivity to roughness and tortuosity of pore channels. The present results can contribute theoretically and practically to the development of the hydrodynamic separation methodology and to determine the effective range of HDC method.

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