Effective Transport Properties in Random Packings of Spheres and Agglomerates

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A modelling framework for the prediction of effective properties in random packings of particles is presented. Random packings of spheres and agglomerates of spheres are numerically generated by using packing algorithms. Effective properties of both the types of packings are evaluated through a Monte-Carlo random-walk (a.k.a. mean square displacement) method, which allows the calculation of both geometrical parameters (e.g., pore size distribution, specific surface area) and transport properties (e.g., effective gas diffusivity, permeability). The results are reported as a function of porosity in dimensionless form, in order to obtain scale-independent information. The effective properties obtained for random packings of spheres are compared with independent experimental data showing a satisfactory agreement. Effective properties of packings of agglomerates are also evaluated, showing that particle agglomeration significantly increases the mean pore size while reducing the effective gas diffusivity and the specific surface area. The results show that agglomerates can not be generally assimilated to spheres with an equivalent diameter. The modelling approach presented in this study may improve the quantitative characterization of porous media composed by aggregates of particles.

1. Introduction

The study of porous media and particulate systems is a classic topic of chemical engineering with broad applications in heterogeneous catalysis, membrane science, pharmaceuticals and packed towers just to cite the most common areas. One of the most important goals consists in predicting and correlating the effective properties of the medium, such as the permeability or the specific surface area, to its basic characteristics, such as the porosity and the particle size (Bertei and Nicolella, 2011a). Effective properties are related to the specific function that the porous media has to perform: for example, in a porous catalyst the effective diffusivity, the pore size distribution and the specific surface area are correlated to the transport properties of the pellet and to the resulting reaction rate of the reactant.

In the last decades, modelling and reconstruction techniques have supported the developments made in the characterization of porous media. Some porous solids have been assimilated to random packings of spherical particles (Bertei and Nicolella, 2011b). This assumption does not hold when, due to the adhesion properties of the materials, particles tend to aggregate in agglomerates and clusters (Fadda et al., 2009). Particle agglomeration is particularly significant when dealing with micro- and nano-particles, for which undesired aggregation may have detrimental effects on the functionality of the system.

In this study, a modelling framework for the numerical reconstruction and characterization of random packings of spherical particles and agglomerates of spheres is presented. The effect of particle agglomeration on effective properties in a wide range of porosity is assessed. In Section 2 the model, consisting of a packing algorithm and a Monte-Carlo random-walk method, is presented. In Section 3, effective properties in random packings of spheres and agglomerates of spheres are shown and discussed. Conclusions are reported in Section 4.

2. Modelling

2.1 Structure generation

Samples of random packings of spherical particles and agglomerates of spheres are numerically generated by using specific packing algorithms. Due to the different particle shape, different algorithms are used to represent the physics of the particle arrangement.

Random packings of spherical particles of equal diameter d are generated through the sedimentation algorithm (Visscher and Bolsterli, 1972), also known as drop-and-roll algorithm, which mimics the deposition of particles into a box. One particle at a time is dropped into a domain of specified dimensions from a random position at the top of the box. The falling particle rolls over one or two already packed particles without friction or inertia until either it touches the bottom of the domain or it is stably supported by three other particles. As the particle comes into rest, a new particle is dropped, repeating the procedure until the domain is completely filled. A portion of a random packing of spherical particles is represented in Figure 1a.

Agglomerates are defined as an assembly of 13 spheres of equal diameter d positioned as in Figure 1b. The number of spheres and their configuration were chosen as a reference to represent an aggregate of almost spherical and regular shape with an agglomerate size of about 3 sphere diameters. The apparent diameter L_a of the agglomerate is equal to $2.732 \cdot d$, the equivalent diameter (i.e., the diameter of the equivalent sphere with the same surface/volume ratio) $L_e = 1.478 \cdot d$, the sphericity is 0.644. Random packings of agglomerates are generated by using a modified collective rearrangement method (Nolan and Kavanagh, 1995). In this method, initially the particles are randomly distributed within the domain in overlapping configuration. Overlaps between different particles cause a restoring force and a restoring moment in a direction required to remove the overlaps. At the same time, a stability constraint is implemented: a particle is considered stable if supported by a contacting particle below its centre of mass while experiencing opposite moments in both the horizontal planes. Particles iteratively move, rotate and drop until all the overlaps have been removed and all the particles have found a stable position.

For both the types of packings, sintering effects are simulated by uniformly increasing the size of the particles until the desired porosity is reached (Bertei et al., 2012). Wall effects are avoided by using periodic boundary conditions in the horizontal directions. Three layers of particles at the bottom of the domain are removed in order to extinguish floor effects as observed by Ben Aïm and Le Goff (1967). The packing algorithms provide the centre coordinate of each sphere in the packing, therefore recreating a virtual sample of the microstructure to be used for the calculation of effective properties. Five structures per setting are generated in order to average the results.

2.2 Effective properties

The effective transport properties are evaluated in the reconstructed microstructures through a Monte-Carlo random-walk simulation (Zalc et al., 2004). A tracer is randomly placed within the gas phase wherein it moves following a Brownian motion. At each step, the tracer moves of the free path, which is chosen from an exponential probability distribution centred on the mean free path. When the tracer collides with a solid particle, it is reflected on the surface according to the Knudsen cosine law. After a prescribed amount of time Δt, the displacement R between the initial location of the particle and its final location is measured. The effective diffusivity D^e is calculated from the mean square displacements of thousands of tracers using the Einstein equation (Einstein, 1926):

$$D^e = \frac{\phi \cdot \left\langle R^2 \right\rangle}{6 \cdot \Delta t}$$

(1)

where ϕ represents the packing porosity. For a given diffusion regime, such as bulk diffusion or Knudsen diffusion, the effective diffusivity is related to the bulk or to the Knudsen diffusivity by the ratio between porosity and tortuosity factor as follows (Mason and Malinauskas, 1983):

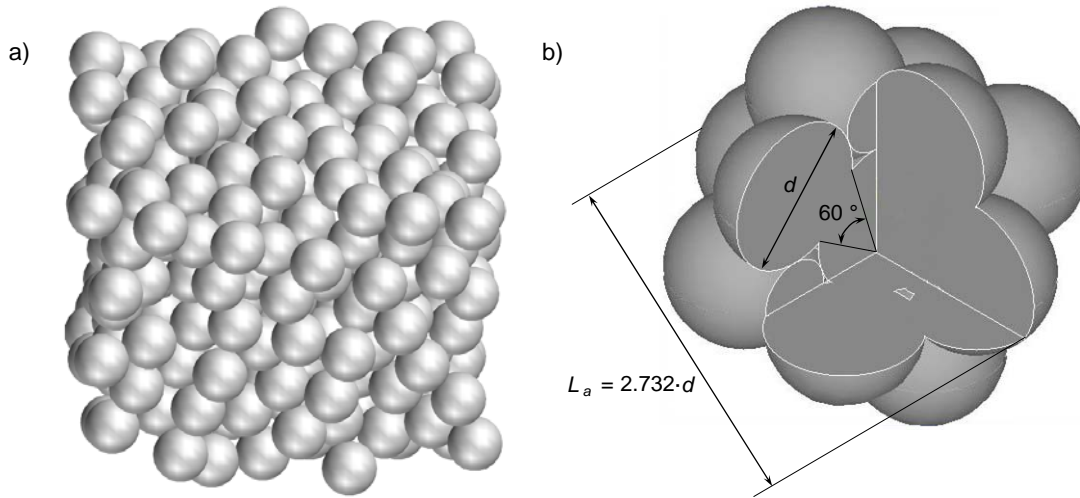$$D_j^e = \frac{\phi}{\tau} D_j \quad \text{with } j = \text{bulk or Knudsen}$$

(2)

Figure 1: a) Portion of a random packing of spherical particles (porosity = 30 %); b) Scheme of the sphere arrangement used to represent an agglomerate of spheres.

Given the Knudsen number, which is imposed in the simulation, Eqs. (1-2) allow the effective diffusivity and tortuosity factor to be evaluated. The ratio ϕ/τ represents the normalized effective diffusivity, independent of the Knudsen regime.

The mean pore size d_p is calculated by using the chord length method (Berson et al., 2011). Chords are lines randomly drawn in the pore space between two solid particles. The mean pore size is calculated as:

$$d_p = \langle l \rangle \left(\frac{\langle l^2 \rangle}{2 \cdot \langle l \rangle^2} + \sum_{m=1}^{\infty} \langle \cos \vartheta_m \rangle \right) \qquad (3)$$

where $\langle l \rangle$ represents the number-averaged chord length, $\langle l^2 \rangle$ the mean-square chord length and $\langle \cos \vartheta_m \rangle$ is the average cosine of the angles between trajectory segments separated by m particle collisions in a random-walk simulation performed in Knudsen regime. The mean pore size is equal to the number-averaged chord length corrected by the statistics of both the chord distribution and the tracer redirecting collisions. Since the mean pore size scales with the sphere diameter d, the dimensionless mean pore size is calculated as d_p/d for both spherical particles and agglomerates.

When dealing with random packings of spherical particles, the permeability B can be evaluated on the basis of the porosity, tortuosity factor and mean pore size as follows (Mason and Malinauskas, 1983):

$$B = \frac{\phi}{\tau} \frac{d_p^2}{32} \qquad (4)$$

Since B scales with the square of the mean pore size, which scales with the sphere diameter d, the normalized permeability is defined as the ratio B/d^2.

The specific surface area exposed to the gas phase per unit volume, S, is evaluated by randomly generating hundreds of test points on the surface of each sphere. The position of the test point is then checked against other particles: if the distance of the test point from the centre of another sphere is smaller than the sphere radius, the test point is internal to the packing. In the other case, the test point is exposed to the pore space, thus it is accounted for in the calculation of the exposed area. It is noteworthy that, in both random packings of spherical particles and agglomerates, there are not closed pores in the range of porosity investigated in this study. The pore percolation was determined using a grid-based

technique (Kenney et al., 2009). The effective exposed area is equal to the number fraction of accepted test points times the particle surface area. The specific surface area is obtained by summing up the exposed area of each particle and dividing by the packing volume. The specific surface area per unit volume is normalized by multiplying S by the sphere diameter, i.e., $S{\cdot}d$, for both spherical particles and agglomerates.

3. Results and discussion

3.1 Mean pore size

Figure 2 shows the normalized mean pore size as a function of porosity in random packings of spheres and agglomerates. For both the types of particles, the pore size decreases as the porosity decreases. The mean pore size in random packings of agglomerates is, in average, 1.7 times larger than the mean pore size in random packings of spherical particles. Such a ratio is smaller than 2.732, which would arise if the agglomerates behaved as spherical particles with apparent diameter $L_a = 2.732{\cdot}d$ (see Figure 1b). Thus, the mean pore size in agglomerates is smaller than what could be expected, due to the effect of the inlets, represented in Figure 3. In fact, the chords traced within the inlets contribute to reduce the number-averaged chord length in Eq. (3), therefore reducing the mean pore size if compared with an equivalent sphere of diameter L_a.

3.2 Effective diffusivity and permeability

Figure 4a shows the normalized effective diffusivity (that is, the ratio between porosity and tortuosity factor) as a function of porosity in random packings of spheres and agglomerates. Experimental data on random packings of glass spheres obtained by Currie (1960) are also reported, which agree with simulation results for spherical particles.

The normalized effective diffusivity is independent of the particle size. For both the types of packings, the normalized effective diffusivity increases as the porosity increases. However, the effective diffusivity in packings of agglomerates is smaller than in packings of spherical particles. This means that the tortuosity factor of packings of agglomerates is larger than in packings of spheres. This result is in agreement with the results discussed above regarding the mean pore size: the inlets create more tortuous paths than in an equivalent packing of spheres.

Figure 4b shows the normalized permeability as a function of porosity in random packings of spheres. Simulation results are compared with experimental data obtained by Bosl et at. (1998) in random packings of sintered glass beads. The Carman-Kozeny correlation (Epstein, 1989) is reported in solid line. The normalized permeability rapidly increases as the porosity increases. The agreement between the two series of data and the Carman-Kozeny equation over a wide range of porosity provides the validation of the proposed modelling framework for spherical particles. On the other hand, validation for agglomerates is not possible due to the lack of experimental data.
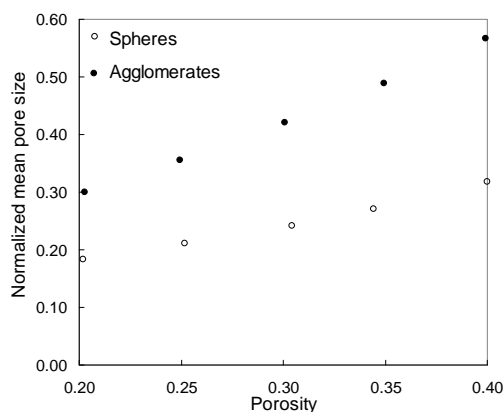

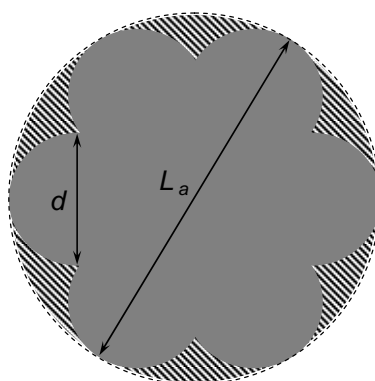Figure 2: Normalized mean pore size as a function of porosity for packings of spheres and agglomerates.

Figure 3: Projection of an agglomerate: the dashed areas represent the inlets with respect to the apparent bounding sphere (marked with a dotted line).
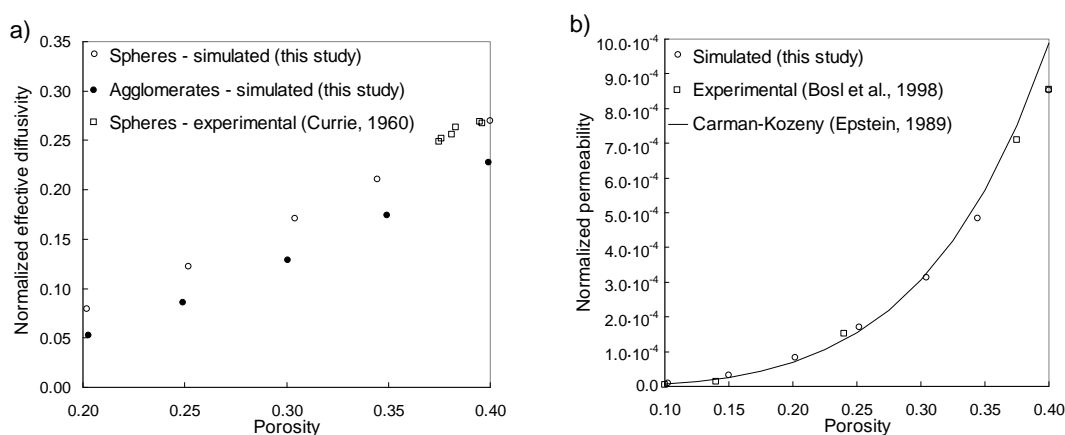

Figure 4: a) Normalized effective diffusivity as a function of porosity for packings of spheres and agglomerates; b) Normalized permeability in random packings of spherical particles.

3.3 Specific surface area

Figure 5 shows the normalized specific surface area per unit volume as a function of porosity in random packings of spherical particles and agglomerates. For both the types of particles, the surface area per unit volume decreases as the porosity decreases. This is due to the larger overlaps, created as the porosity decreases, which reduce the particle surface area exposed to the gas phase. This phenomenon is predominant if compared with the increase in the number of particles per unit volume as the porosity decreases, which would lead to increase the specific surface area.

The results clearly show that particle agglomeration reduces the specific surface area if compared with spherical particles of the same size d. It is interesting to note that the packings of agglomerates have almost the same specific surface area of packings of spherical particles with diameter equal to the equivalent agglomerate diameter L_e. On the other hand, if agglomerates were assimilated to spheres of diameter L_a, the specific surface area would be underestimated of about 45 %.

4. Conclusions

This numerical study showed that particle agglomeration significantly affects the effective properties in random packings of particles even if agglomerates retain almost a spherical shape. Particle agglomeration leads to an increase in the mean pore size while the effective diffusivity and the specific surface area per unit volume decrease. The results show that it is not generally possible to assimilate agglomerates to spheres with an equivalent diameter, suggesting that particle agglomeration must be properly taken into account and characterized.

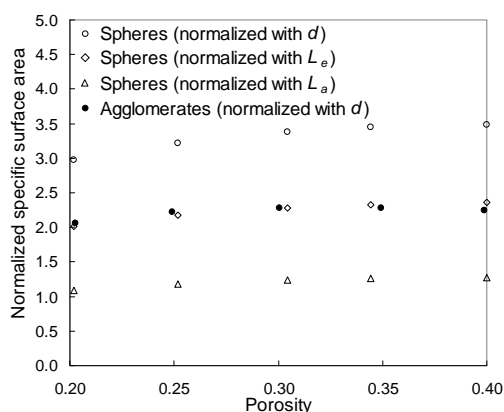Further research will focus on different agglomerate configurations and particle shapes.

Figure 5: Normalized specific surface area as a function of porosity for packings of spheres and agglomerates.

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