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A Monte Carlo integration method to determine accessible volume, accessible surface area and its fractal dimension

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ABSTRACT

We present a self-consistent Monte Carlo integration scheme to determine the accessible volume and the accessible surface area of a porous solid with known atomistic configuration. The new feature of this method is the determination of the variation of volume not only with respect to the distance from the surface (geometrical factor) but also with respect to the energy of the closest solid atom type. The variation with respect to distance gives us information about the area of the solid–fluid boundary (which is defined as one on which a spherical particle has zero solid–fluid potential energy) while the variation of the interfacial area of a contour at any distance from the surface, yields the surface curvature, for both convex and concave surfaces. On the other hand, the variation with respect to the type of solid atom yields information about the distribution of the area in terms of the heterogeneity of the surface. We illustrate our new method with a number of examples, ranging from a simple channel pore to complex solids, such as metal organic frameworks (MOF) and bundles of carbon nanotubes.

1. Introduction

Surface area and pore volume of porous solids has been a subject of immense interest in physical characterization [1–3]. Although it is not strictly correct, they have been extensively used as an indicator on how good an adsorbent is [4–13]. One of the popular methods frequently used for surface area determination is the BET method [5]. Although other methods can be used to obtain the surface area [14,15], this remains the method of choice because it is simple and quick, although its assumptions are not readily satisfied by all practical solids and modern advanced solids such as metal organic frameworks. Two methods are normally employed to determine the void volume: one is the helium expansion method and the other is based on adsorption of a subcritical fluid (such as argon and nitrogen) at the saturation vapour pressure. The first method usually assumes no adsorption of helium and the second method assumes that the adsorbed phase has the same density as the liquid adsorptive. Both of these present problems: for example helium adsorbs in fine pores and the assumption that the adsorbed phase behaves as liquid lacks credibility as it is well-known that the adsorbed phase can be denser than the liquid phase because of the external field due to the adsorbent.

The objective of this paper is to present a new method based on Monte Carlo integration to determine the accessible volume and accessible surface area, for crystalline solids with known atomic configuration. Besides these two structural parameters, this new method is used to calculate the distribution of the surface area according to the different type of solid atoms in the configuration and also the fractal dimension as a structural parameter to quantify the roughness of the surface.

2. Theory

The method to determine the accessible volume is similar to that presented earlier [16]. In this paper we present a modification to that method in which we collect information about the variation of the accessible volume with distance from the surface. The derivative of the accessible volume with distance is simply the area with respect to distance. This gives us the interfacial (solid–fluid) accessible surface area, and also shows how the pore curvature changes. The interfacial (solid–fluid) accessible surface is defined as the boundary on which the solid–fluid potential energy of a fluid particle is zero. Before discussing our new methodology, we review briefly the Monte Carlo method to determine surface area that is available in the literature, and discuss its problems.

2.1. Previous Monte Carlo method to determine accessible surface area

For solids with known atomistic configuration, such as metal organic frameworks, the Monte Carlo integration method can be used to obtain the geometrical surface area which is essentially the area traced by the centre of a sphere rolling over the solid surface [17,18]. The yardstick of this measurement is the size of the

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sphere. If the sphere rolls over the surface, such that the distance between the centre of this sphere and the centre of the closest solid atom is σ_{sf} (cross collision diameter between the adsorbate molecule and the solid atom, $\sigma_{sf} = (\sigma_{ss} + \sigma_{ff})/2$), this surface area is called the hard sphere surface area. A special case of this is when the size of the test sphere is zero, the resulting surface is known as the Connolly surface [19].

Let us now discuss the traditional Monte Carlo scheme to determine the geometrical surface area and point out the problem with this approach. For a given solid atom, say atom k, the possible locations of the centre of a probe particle are on the surface of a sphere whose centre is the same as the centre of the solid atom "k" and the sphere radius is σ_k. Thus the maximum possible geometrical surface area contributed purely by this solid atom is the area of the sphere $(4\pi\sigma_k^2)$. However, not all this area is accessible to a probe particle because of the neighbouring solid atoms. To determine the accessible area we choose a point on this sphere of radius σ_k at random, place the centre of a probe particle at this point and compute its potential energy with the solid (i.e. all the solid atoms). If this is positive the selection of this point is a failure; otherwise it is a success. We repeat this process many times, and at the end of the process the fraction of successes, g_k, is calculated. The accessible area associated with this solid atom is $g_k\,(4\pi\sigma_k^2)$. We continue this process for each solid atom in sequence until we have accounted for all solid atoms. The total geometrical surface area is $S_{geo} = \sum_k g_k\,(4\pi\sigma^2)_k$, where k denotes the kth solid atom (the heavy red line in Fig. 1a).

That seems to be simple enough, but there is a difficulty with this approach because the accessible area with respect to the solid atom k is $g_k\,(4\pi\sigma^2)_k$. This is the area associated purely with this kth solid atom because of the choice of the surface of the σ_k- sphere. The correct area for sampling is actually smaller because in the presence of the surrounding solid atoms the molecular probe can probe slightly deeper into the kth atom (red line Fig. 1b). Although this correction is very small, the incorrect determination of the zero potential surface can give substantial errors in the determination of surface area. This is the case for narrow pores whose size is comparable to the size of the probe molecule. We test this with the characterization of a 0.69 nm slit pore and the results show a difference of 17% between these two methods. In addition, it is worthwhile to develop a consistent generic method and this can be built-in with the process of determination of accessible volume that we will describe next. It allows us to determine the accessible volume and the accessible area in the same process, making the determination of all solid properties in a self-consistent manner. Furthermore by doing this, we can reduce the computation time for the determination of the accessible pore volume and surface area.

2.2. The methodology for accessible volume and accessible surface area

The accessible pore volume is defined as the volume accessible to the centre of mass of the adsorbate particle at zero loading. For solids whose atomistic configurations are known (such as crystalline solids), this can be determined with the integration Monte Carlo method [16]. For the purpose of characterization, a simple molecular probe is chosen (even though the method that we will describe works for all adsorbates). Noble gases are the best candidate for this, and argon is the logical choice because it is readily available. The choice of noble gas is appropriate for solid characterization because it is inert, spherical and non-polar. Nitrogen is also a good candidate and is the most widely used adsorptive because it is cheaper than noble gases, but in terms of adsorption it is more specific for electrostatically charged sites because it carries a quadrupole moment and therefore favours high affinity functional groups.

The Monte Carlo procedure for finding the accessible volume and accessible surface area is as follows: we insert a particle at a random position in the simulation box, which is the representative sample volume of the solid for which we would like to determine the accessible volume. After this insertion, we calculate its potential energy with the solid by summing all pairwise potential energies between this test particle and all solid atoms, and then remove it from the box to simulate the zero loading condition. If

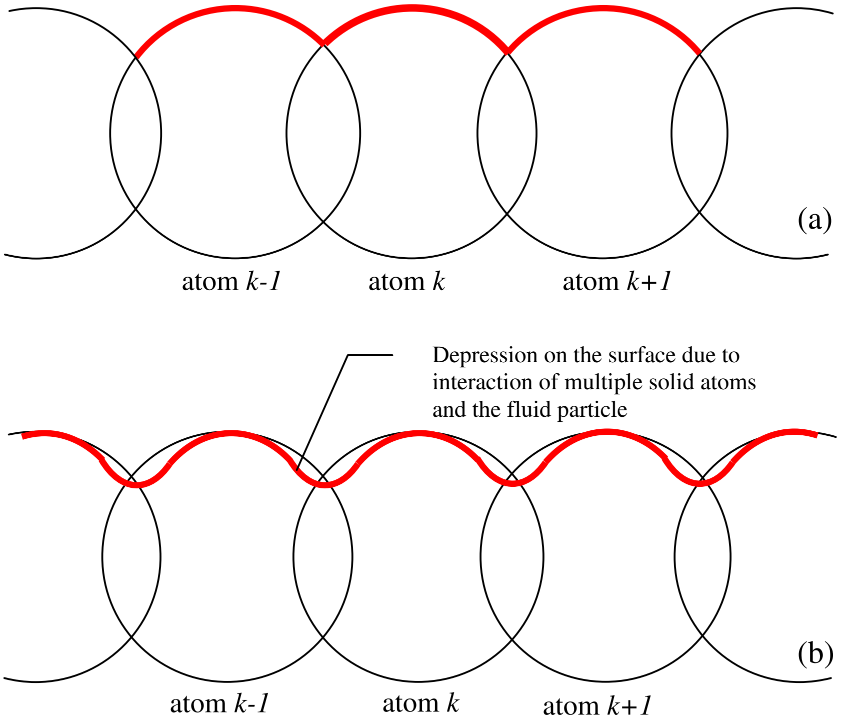

Fig. 1. The approximate and actual geometrical surface areas. The approximate surface area of atom k is given by the heavy red line while the dashed line shows the actual surface area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)