NEW CAPABILITIES FOR GEOMETRICAL ANALYSIS OF THE COMPUTER MODELS OF COMPLEX SYSTEMS

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The extraction of physical information from the computer simulation needs a quantitative analysis of the model. However, it is not so easily to extract the necessary characteristics from the model, especially if the model consists of thousands particles. To calculate the penetration properties, permeability or accessible volume for a given diffusiant needs the analysis of the model structure. In particular, one should study unoccupied volume distribution, bottleneck radii and potential paths through the sample for a given probe.

A rigorous geometrical approach to study structure is based on the Voronoi-Delaunay tessellation. Of a special interest for us is the Voronoi network, i.e. the network of all edges and vertices of the Voronoi polyhedra of all atoms of the system. This network penetrates unoccupied space inside system and plays the role of a "navigation map". Every site (vertex) of the Voronoi network is the center of the interstitial sphere and determines the "deepest" location between the atoms. Each bond of the network is a "fairway", along which one should move a probe of the maximum radius between two sites [1] and [2].

The penetration properties and permeability of dense packings of monosized spheres had been calculated in [1] and [3]. However, a wide class of systems (polymers, colloidal systems) should be modeling by particles of different size, moreover by the significantly overlapping ones. The generalization of the Voronoi-Delaunay approach to any ensemble of polydisperse spherical particles have been done in [2] and it was applied to create models of dense packings of polydisperse spheres [4].

Now we use this geometrical method to analyze the accessible volume inside the model of glassy atactic polypropilene and models of low density packings of identical spheres modeling a carbon black and aerosil.

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The model of polymer was constructed by the Monte Carlo method as an ensemble of chains of partly overlapping spheres of three different diameters (2.0, 1.8 and 1.3 Å) — see [5]. Geometrically, the accessible volume is the volume inside the sample, where a probe of a radius R_t can freely move (or at least be placed). One should distinguish two different cases. First, one can speak about the total accessible volume, which includes all blocked pores. We were dealing with this case when calculated the chemical potential by the Widom method — see [6]. On the other hand, from the view point of experimental porometry, the volume is accessible if it is achievable by a probe from the sample surface. This volume is obviously defined by a percolative cluster of the accessible pores. We calculated the accessible volume distribution inside the model box for a different size of the probe. The diffusiant with the radius value less then 0.75 Å can go through our polymer. There are only localized pores for the larger probe.

The accessible volume for low dense packings as a function of a probe radius R_t is demonstrated in Figure 1. The solid lines specify the volume fraction of percolative cluster. It always begins with some critical value of probe radius R_c. The dotted lines concern to the fraction of the total accessible volume. It begins with a larger value of R_t and increases monotonously with decreasing R_t. At small values of the probe radius ($R_t = 0$) it tends to the whole volume of the interpartical space determining the porosity of the system.

Model I represents an usual dense noncrystalline packing of 5488 identical particles inside a model box with the periodic boundary conditions [7]. Models II and III are contain 4107 and 1968 particles and were created from model I by removing some atoms. All particles in the models are in contact (consolidated) with a few nearest neighbors. From this point of view one can consider that our models are "rigidly built". The value of the porosity of these models are estimated as 0.30, 0.48 and 0.75, respectively.

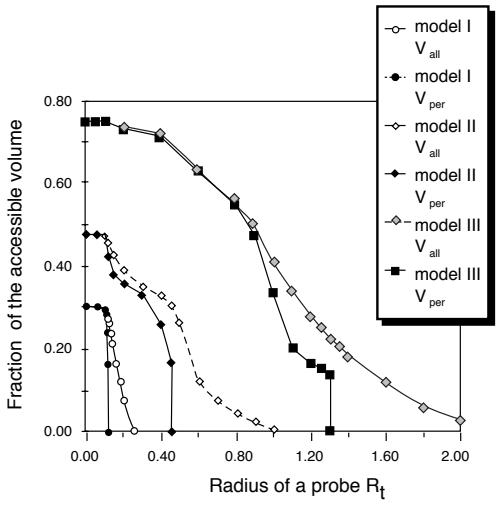

Figure 1

Fraction of the accessible volume inside various packings as a function of a probe radius R_t. The solid lines specify volume of percolative cluster (the volume, which is accessible for a probe from the surface of the sample). The dotted lines show the total accessible volume (including the blocked pores, where the probe could be placed). At $R_t = 0$ it gives the value of porosity of the system. Model I is a dense noncrystalline packing of 5488 particles. Models II and III contain 4107 and 1968 particles, they are created from model I by removing of some particles.

The pores inside the dense packing (model I) are mainly the cavities between tetrahedral and octahedral configurations of particles (micropores). Notice, that the volume of the percolative cluster tends here to the total accessible volume after a small reduction of the probe size compared to the critical value. The other situation takes place for the low density system (model III). Here we observe the pores, whose size is several times larger than the diameter of the particle (mesopores). The volume of the percolative cluster differs from the total accessible volume in the appreciable interval of R_t value. The micropores (pores of radius in interval 0.1-0.2) are not manifested. Model II demonstrates the intermediate behaviour. Rather large pores are accompanied by the micropores.

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