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Infiltration Non-Wetting Liquids into Nanoporous Media at Different Initial Degree of Filling

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Abstract

The paper presents a physical model can qualitatively explain the observed experimental dependencies of reducing the pressure of the second and subsequent filling of partially filled porous medium. The model is based on an approach based on the fact that the pores in the porous medium is a chaotically arranged spherically shaped voids. If liquid is leaking out of such an environment is the formation of clusters associated with a liquid meniscus at the interface with air. Upon subsequent filling of the disappearance of the menisci is energetically favorable process that leads to a reduction in filling pressure.

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1. Main text

Filling of hydrophobic nanoporous media by non-wetting liquids has been being investigated for a long time. Practical interest in such systems is related to their high specific energy efficiency. At sufficiently developed specific surface area of the medium the absorbed energy can reach 10J per kg, which is several orders of magnitude superior to traditional damping materials, shape-memory materials and composite materials [1]. For the most of the studied porous media at the first filling and subsequent removal of excess pressure it was found that the liquid does

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not outflow and can remain in porous media. Moreover, a similar phenomenon is observed for both quasi-static and impulse pressure variation. In addition, there are several reasons of non-outflow and found that residuary volume changes over time in the direction of decreasing. Such effects are extremely interesting from a theoretical point of view, because in recent years conditions and properties of disordered media such as glasses, colloids, granular media, and others have been actively investigated. [2-3]. A major role in such media plays clusters formations, as they determine the properties of disordered media.

This paper studies the effect of the observed [4] reducing the pressure of the second and subsequent filling of the disordered porous medium by non-wetting liquid if the liquid partially remain in the previous cycle. Studied in the paper porous medium is a porous glass Vycor [4]. This effect is not a specific feature for porous glasses, because it was observed for the ordered and disordered porous media with different pore size distribution, however, it was not investigated and explained. An approach to the description of the observed phenomenon is suggested, which takes into account the emergence of local configurations of clusters of fluid and their interaction within the infinite percolation cluster-filled pores. This approach allowed us to qualitatively explain the observed infiltration pressure drop.

The proposed approach is described in detail in [5], the essence of which is as follows. A pore can only be in one of two possible states: either be filled (on the assumption of there are paths for fluid to that pore or otherwise be available to fill, if no path), or empty. The probability of such a state is determined by the work that must be done to fill the pores by the fluctuation. "Quantum" of filling at quasi-static case is considered the filling of one pore (because the throats volume is negligible compared with the whole volume of pore [6]). If we write δA_{in} as the minimum work that must be done to fluctuation fill the pore radius *R* by non-wetting liquid, the normalized probability of finding that the pores in the filled or empty state can be represented as:

$$w_{in}\left(\delta A_{in}\right)=\left[1+\exp\left(\frac{\delta A_{in}}{T}\right)\right]^{-1}$$

Depending on the pressure and the degree of filling of the medium when $\delta A_{in} < 0$ the probability $w_{in} \sim 1$ and liquid fills the pore and the disappearance of existing meniscus in his throat of neighboring pores in the partially filled environment and the formation of new points of contact in the filled pores with empty pores are occured, on the assumption of that liquid can flow to them. If $\delta A_{in} > 0$, then $w_{in} = 0$, and pore remains empty.

Pore in the porous medium is filled only in the case when liquid can penetrate to it. Under the above assumptions condition of penetration can be achieved through the formation of an infinite cluster-filled pores. In this case, only those pores can be filled, which belong to the infinite cluster shell of filled pores. If we neglect the elastic compression then, the work δA_{in} of filling a spherical pores in the shell of an infinite cluster-filled pores in the case of a narrow pore size distribution can be written in a form [5]:

$$\delta A_{in}\left(p,R,\theta\right)=-pV+\delta\sigma(1-\eta)S+\sigma\eta SW(\theta) \tag{1}$$

where η is the connection coefficients equal to the ratio of the total area of menisci in the throat with the neighboring pores to the surface area of the pore. Here σ is surface energy of the liquid, $\delta\sigma=\sigma^{sl}-\sigma^{sg}$ - the difference between the surface energy of the interface between the solid –liquid σ^{sl} and solid – gas σ^{sg}, $S=4\pi R^2$ is surface area pore radius *R*, value $W(\theta)$ takes into account the interaction of the liquid nanoclusters neighboring pores and is defined as the difference between the average number of meniscuses before and after filling the pore, per nearest neighbor. The product $W(\theta)$ on the surface energy of the liquid in the meniscus determines the possible change in the energy of the "many" nanocluster fluid interaction with the cluster of fluid in the neighboring pores during infiltration liquid into the pore. Under the interaction energy of nanoclusters fluid meant keeping energy mutual arrangement of filled and empty pores in contact with the considered por, and hence the surface energy of the meniscus. Value $W(\theta)$ is determined as follows [5]: