An analysis of aggregate response of confined liquids in nanoenvironment

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Based on a dimensional analysis of flow rate in nanoenvironment, the aggregate response of a nanoporous particle subjected to a dynamic pressure is studied in context of effective phase transformation. The numerical results indicate that in the early stage the system behavior is mostly determined by the nucleation and associated growth of saturated pore clusters (SPCs), while in the late stage the SPC coalescence becomes predominantly important. The relations between the absorption time and the sizes of the particle and the pores are highly nonlinear.

Keywords: nanoporous, confined liquid, infiltration, pore clusters, number density

1. Introduction

In the past decade, the rapid progress in processing techniques has greatly promoted the development and use of nanoporous particles and membranes. These materials are used in various applications such as catalyst supports, membrane separation in ultrafiltration and reverse osmosis, and drug delivery systems [1–5]. The nanoenvironmental properties of these materials are highly different from those observed at the macroscopic level. According to the nuclear magnetic resonance (NMR) analysis, the molecular diffusion in the vicinity of the solid–liquid interface is higher than that in the interior of a nanoporous material [6–8]. Consequently, there exists a significant size effect, i.e., the confined flow is affected by the pore radius. Due to the influence of molecular mobility, the distribution profile of a specific component can also be dependent on the particle size or membrane thickness [10].

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While a variety of experimental data of the confined liquid behavior can be found in open literature (e.g., [6–10]), since the measurement results are quite sensitive to the processing and testing conditions, very often the data from different research teams do not agree with each other quantitatively. Furthermore, even if the confined liquid in a single nanopore were fully understood, there is still no satisfactory model that can relate the molecular behaviors to the micro-mechanical analysis of the system response.

A nanoporous particle or membrane can be considered as a three-dimensional, interpenetrating nanovoid-surrounding network, with the characteristic length ranging from 1 to 1000 µm. Due to the high specific area around 100–1000 m²/g, the ordinary percolation theories cannot capture the nonlinear and size dependent nature. In view of the above considerations, in order to provide a scientific basis for developing the next generation intelligent catalysts with the adjustable surface/interface properties, in this paper we will establish a multiscale model to study the aggregate system performance. We study the wetting process in a nanoporous particle immersed in a liquid subjected to an increasing pressure. The system response is characterized by the absorption time, $t_a$, which is essential to the assessment of design variables of precision reaction control. Since the particle size is much larger than the pore size, the particle is assumed to be homogeneous and isotropic.

Effective phase transformation

In a nonwetting liquid, initially the solid and liquid phases are separate. As the pressure increases or the collected state, the energetically favorable inflow starts. Due to the large pore volume fraction and the high connection density, this process can be considered as an effective phase transformation from empty pore clusters (EPCs) to saturated pore clusters (SPCs) [11–13], as depicted in figure 1. If the pressure is sufficiently high and the pore size distribution is narrow, the capillary effect can be overcome fully and the factor of the pore radius comes in by affecting the inflow rate instead of determining whether or not the inflow can occur. The boundary of a SPC can be fractal yet the interior is filled, and thus in the following discussion we consider only the average behavior.

Under the relatively high pressure, the liquid penetrates into the particle surface at a number of sites, which are referred as the nucleation sites of SPCs. As the liquid flows into the adjacent pores, the SPC expands along both radial and circumferential directions, and at meanwhile new SPCs are nucleated continuously. While it is clear that wetting is easier in larger pores and these places are more likely to serve as nucleation sites, other factors such as the precursor film formation and the dependence of contact angle on flow direction, even thermal fluctuations, can be important at the nm level. Thus, in the current research, the SPC nucleation will be collectively considered as a random process.