

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.

KEY WORDS: nanoporous, confined liquid, infiltration, pore clusters, number density

1. Introduction

In the past decade, the rapid progress in processing techniques has greatly promoted the use of nanoporous particles and membranes in advanced reaction control, reversible and/or selective chemisorption, etc. [1–5], and the associated catalytic activities in a variety of liquids such as toluene, cumene, octane, and benzyl/acetylene/polyfurfuryl alcohols has become an active research area. At the nm scale, the behavior of the liquid confined in nanopores is quite different from that observed at the macroscopic level. According to the nuclear magnetic resonance (NMR) analysis, depending on the nature of the atom–atom interaction, the mobility of the molecules near the solid–liquid interface can be either higher (superdiffusive) or lower (subdiffusive) than that in the interior [6–8]. Consequently, the average diffusion distance can be stated as a two-power-law function [9]. Usually, the thickness of the interface zone is in the range of 1–5 nm. In a nanopore with the pore size comparable with this value, 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 of 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 m^2/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.

2. Effective phase transformation

In a nonwetting liquid, initially the solid and liquid phases are separate. As the pressure increases to the critical value, 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 points, 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.

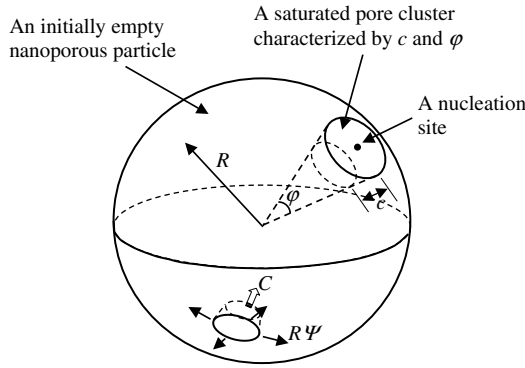


Figure 1. A schematic diagram of the effective phase transformation in a nanoporous particle.

The concept of number density can be employed to describe the SPC population. In this framework, each SPC is characterized by its radial depth, c , and opening angle, φ (see figure 1). The evolution of the SPC number density is governed by

$$\frac{\partial n(c, \varphi, t)}{\partial t} + \frac{\partial [C(c, \varphi, t)n(c, \varphi, t)]}{\partial c} + \frac{\partial [\Psi(c, \varphi, t)n(c, \varphi, t)]}{\partial \varphi} = n_N(c, \varphi, t) + n_c(c, \varphi, t), \quad (1)$$

where $n(c, \varphi, t)$ is the number of SPC of size $\{c, \varphi\}$ at time t per unit volume, and n_N and n_c are the average SPC nucleation and coalescence rates, respectively. The last two terms at LHS reflect the influences of SPC growth, with C being the radial growth rate and Ψ being the circumferential growth rate.

The average growth rates should be proportional to the flow rate in the nanopore, v , which is a function of pressure p , liquid density ρ , wetting driving force $\Delta\gamma$, and, as discussed above, pore radius r . The driving force of wetting can be taken as the difference between the interfacial tension and the surface energy of the network material. Note that for a system where $r \approx 10\text{--}100$ nm, $v \approx 100$ m/s, and the viscosity coefficient $\nu \approx 10^{-7}$ m²/s, the Reynolds's number $Re \gg 1$. Hence, following the classic two-power-law relation, through the dimensional analysis we have $v = \alpha'' \sqrt{p/\rho} (pr/\gamma)^{\beta'} + \alpha' \sqrt{p/\rho} (pr/\gamma)^\beta$, where α'' , β' are system parameters associated with the normal flow, and α' , and β are related to the interface flow, respectively. When $r \rightarrow \infty$, the second term should vanish and the first term should converge to the result of the Bernoulli's equation, $v \propto p^{1/2}$. Therefore, β' is set to 0 and α'' can be taken as $\sqrt{2} (1 - d/r)^2$, where d is the effective thickness of interface zone. Similarly, α' can be considered as $\alpha [1 - (r - d)^2/r^2]$, with α being a material constant. The average SPC growth rates in a porous particle with the pore size distribution function of $P(r)$ can then be stated as

$$C = \int_0^\infty P(r) \left\{ \left(1 - \frac{d}{r}\right)^2 \sqrt{\frac{2p}{\rho}} + \alpha \left[1 - \left(\frac{r-d}{r}\right)^2\right] \sqrt{\frac{p}{\rho}} \left(\frac{pr}{\gamma}\right)^\beta \right\} dr \quad (2)$$

and $\Psi = 2C/(R - c/2)$.

The average SPC nucleation rate, n_N , is proportional to the number of available nucleation sites,

$$n_N(c, \varphi, t) = \eta_0 P(c) P(R\varphi) \left[1 - \frac{1}{4\pi R^2} \iint n(c, \varphi, t) \cdot \zeta \varphi^2 R^2 dc d\varphi \right], \quad (3)$$

where R is the particle radius; ζ is a geometry factor, which equals π for regular shaped SPCs; $\eta_0 = \eta_1 \int_0^{r_{cr}} P(r) dr$, with $r_{cr} = 2\Delta\gamma/p$ being the critical pore size and η_1 a parameter dependent of time resolution.

The average SPC coalescence rate, n_c , on the other hand, is determined by the probability that the summation of the sizes of two adjacent SPCs equals the distance between them, i.e.

$$n_c(c, \varphi, t) = N(t) [\tilde{n}_c(\varphi, t) - 2\hat{n}_c(\varphi, t)]_{c=\frac{\zeta}{\varphi}}, \quad (4)$$

where $N(t) = \iint n(c, \varphi, t) dc d\varphi$ is the total SPC number, \tilde{n}_c is the probability of forming a large SPC, and \hat{n}_c is the probability of the disappearance of a small SPC. According to the principal of conditional probability,

$$\tilde{n}_c(\varphi, t) = \frac{2}{N} \int_0^\varphi g(x/\pi R) \left\{ \int_0^{\frac{\varphi R-x}{2}} n_0(\tilde{\varphi}, t) \left[1 - (1/N) \int_0^{\varphi R-x-\tilde{\varphi}} n_0(\hat{\varphi}, t) d\hat{\varphi} \right] d\tilde{\varphi} \right\} dx, \quad (5)$$

$$\hat{n}_c(\varphi, t) = \frac{1}{2} \int_0^\pi \left\{ \tilde{n}_c(\hat{\varphi}, t) [n_0(\varphi \leq \hat{\varphi}, t) + n_0(\hat{\varphi} - \varphi, t)] \right\} / \int_0^\varphi n_0(\tilde{\varphi}, t) d\tilde{\varphi} d\hat{\varphi}, \quad (6)$$

where $n_0(\varphi, t) = \int_0^R n(c, \varphi, t) dc$, and $g(\hat{x}, t) = \xi \sqrt{N} (1 - \hat{x})^{\sqrt{N}-1}$ is the probability that two adjacent nucleation sites are $\hat{x} = x/\pi R$ apart, with ξ being the normalization coefficient.

Equations (1)–(6), together with the initial condition of $n(c, \varphi, 0) = 0$ and the boundary condition of $n(0, 0, t) = 0$, provide a convenient framework for analyzing the effective phase transformation in the porous particle or membrane. When the total SPC volume increases to the particle/membrane volume, the saturation is reached and the absorption time, t_a , can be calculated accordingly.

3. Discussion

Figure 2 shows the numerical results of the evolution of $n_0(\varphi, t)$. The pore size distribution is described by a lognormal function with the mean value $\bar{r} = 100$ nm. The pressure difference is assumed to be 10^4 MPa, and $\Delta\gamma =$

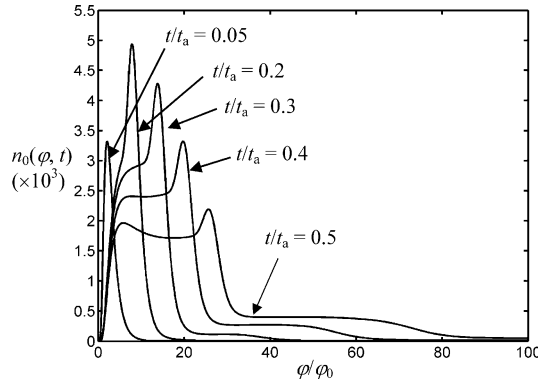


Figure 2. The distribution of the SPC number density integrated over c .

10 mJ/m². The values of d is taken as 10 nm, which is compatible with the NMR data [7]. The characteristic angle $\varphi_0 = r/R$. The nucleation coefficient η_1 is set to 0.001 to obtain a sufficiently fine time resolution. It can be seen that at the early stage when $t/t_a \ll 1$ the n_0 distribution is dominated by the SPC nucleation term n_N and of a quasi-parabolic form, with the peak around \bar{r} . As the SPCs grow continuously, the coalescence is increasingly pronounced and the distribution curve becomes somewhat irregular. A most important phenomenon in this stage is the rapid decrease in n_0 in the low- φ region and the gradual formation of a plateau in the high- φ region. Eventually the n_0 curve consists of two plateaus separated by a narrow “pulse” with the height keeping decreasing. In the late stage of the wetting process, due to the large average SPC size, the system performance is dominated by the SPC coalescence. The low- φ plateau vanishes quickly and finally the high- φ plateau is reduced to a unit delta function at R , indicating the eventual saturation. The evolution process is highly nonlinear. When t/t_a is about 0.4 the largest SPC angle is only around 0.1. At $t/t_a \approx 0.8$, the SPC angle tends to 2π , i.e. a complete, saturated shell has been formed between the EPC and the liquid phase. The shell expands inward with a rate of C and at $t/t_a = 1.0$ arrives at the center of the particle.

The influence of the average pore size \bar{r} and the particle size R on the saturate time t_a is shown in figure 3. The characteristic time t_0 is 1 μ s. As expected, as the pressure difference or the pore size decreases the flow rate in the nanopore, v , is lowered, and as a result t_a becomes larger. The factor of \bar{r} comes in also by affecting the SPC nucleation and coalescence. With a smaller \bar{r} the starting point of SPC growth moves to the low- φ end, which in turn suppresses the coalescence. Increasing R has a similar effect. The magnitude of $\partial t_a / \partial \bar{r}$ is quite high when \bar{r} is relatively small, while when $p\bar{r} / \Delta\gamma$ exceeds about 0.05 the influences of p and \bar{r} are relatively small. Over the ranges of expected variation of these factors, the ratio of t_a/t_0 is around 1–10, which indicates that the assumption of flow rate discussed in Section 2 is self-compatible.

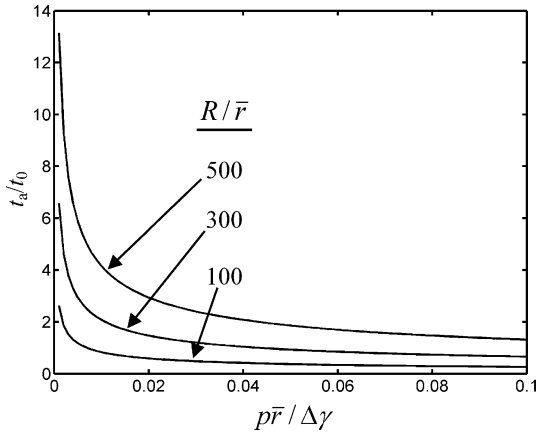


Figure 3. The influences of the pressure difference and the pore size on the absorption time.

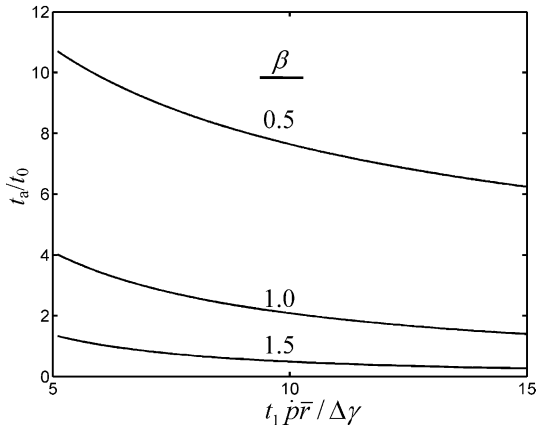


Figure 4. The influences of \dot{p} and β on the absorption time. The characteristic time $t_1 = 1$ ms.

In dynamic working environment the characteristic time of pressure variation can be comparable with or even smaller than the absorption time. Under this condition, the increasing rate of the pressure, \dot{p} , must be taken into account. Figure 4 shows that t_a increases with the decreasing of \dot{p} and β , as it should. The factor of \dot{p} comes in through two mechanisms. Firstly, at a given time, a higher \dot{p} leads to a larger pressure difference, which increases the flow rate. Secondly, as \dot{p} rises, more pores will be involved in the SPC growth and coalescence, i.e. r_{cr} increases. Both of the two mechanisms promote the forced infiltration. However, since the effect of \dot{p} is accumulated over the wetting process, the degree of nonlinearity of the $t_a-\dot{p}$ relation is relatively low compared with that of t_a-p relation (see figure 3).

4. Conclusion

To summarize, a framework has been established to study the aggregate response of nanoporous materials by the analysis of effective phase transformation. The forced infiltration is characterized by the evolution of the number density of SPCs. This model provides a scientific basis for the design of experiments for further study and the first-order system optimization. Clearly, for the final validation of the above discussion the theoretical results must be tested against the experimental data of the degree of saturation. The following conclusions are drawn:

- (1) The evolution of the number density of pore clusters is highly nonlinear due to the complicated nucleation, growth, and coalescence behaviors. At the early stage the n_0-c relation is quasi-parabolic, which then turns into a two-plateau curve and eventually converges to a unit delta function.
- (2) Prior to the final saturation, a saturated shell is formed surrounding the core area of the particle, after which the system behavior resembles that of a spherically symmetric percolation process.
- (3) The absorption time rises as the average pore size or the pressure difference decreases, or as the particle size increases.

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