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# Effective Dewetting in a Microporous Particle

In this paper, the kinetics of the outflow in a microporous particle infiltrated by a nonwetting liquid is analyzed in context of effective phase transformation. The "dewetting" process is considered as the nucleation, growth, and coalescence of empty pore clusters (EPCs) that starts from the interior and eventually involves the whole particle. Initially, the EPC nucleation is dominant while the influence of EPC coalescence becomes increasingly important as the EPC volume fraction increases. The dependence of the dewetting time on the pore size distribution is discussed in detail. [DOI: 10.1115/1.2060734]

### 1 Introduction

Since the beginning of the last century, the application of nanoporous materials in selective catalysis and adsorption processes has been an active research area [1,2]. Usually, nanoporous materials are classified as microporous materials ( $r \le 2$  nm), mesoporous materials ( $2 \text{ nm} < r \le 50$  nm), and macroporous materials ( $50 \text{ nm} < r \le 1000 \text{ nm}$ ), with *r* being the pore size. The microporous materials of ultrahigh specific surface areas are particularly important to chemical, environmental, mechanical, as well as bioscience fields. They are often synthesized in the form of micropowders around  $1-1000 \ \mu m$  diam through templating methods [3]. In the interior of these particles there are threedimensional nanoporous structures, and the surface properties can be adjusted in broad ranges by plasma or thermochemical treatments [4].

In a variety of engineering applications and characterization procedures, the nanoporous particles are immersed in nonwetting liquids, e.g., aqueous solutions of functional chemicals [5,6]. Under a high working pressure, the capillary effect is overcome and the nanopores are filled by the liquid. The associated inflow and diffusion processes have been studied intensively, both experimentally and numerically [7-10]. As the pressure decreases, in a mesopore, the separation of the liquid and the solid can be difficult; that is, there are significant hysteresis loops in sorption isotherm curves, probably due to the difficulty in gas phase formation or the difference between contact angles of intruding and extruding liquids [7,11,12]. In microporous particles, on the other hand, the energetically favorable "outflow" will lead to a complete dewetting at the liquid-solid interface in the nanoenvironment. However, currently, most of the experimental and theoretical investigations in this area are focused on the molecular behaviors in a single nanopore. The studies on the aggregate response of the nanoporous particle are scarce.

In view of the above considerations, in this paper we will develop a pore-cluster model to relate the system performance, such as the dewetting time, to the important global design variables, such as the pore-size distribution. Since the particle size is much larger than the pore size and the orientation distribution of the nanopores is usually random, in the following discussion the confined flow is assumed to be isotropic.

#### 2 Governing Equations

As the external pressure decreases to below the critical value  $p_0$ , the liquid confined in the nanopores in a microporous particle

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becomes unstable and the dewetting starts randomly at a number of points. Note that the critical pressure can be assessed as  $p_0 = 2\gamma/r$ , where  $\gamma = \gamma_{1s} - \gamma_s$ , with  $\gamma_{1s}$  being the solid-liquid interfacial energy and  $\gamma_s$  the effective surface energy of the network material. As the liquid flows out of the porous space surrounding the initiation site, an empty pore cluster (EPC) is formed and it grows along both radial and circumferential directions. Hence, the dewetting process can be considered as an effective phase transformation from filled pore clusters (FPCs) to EPCs. In the early stage, the number and average size of EPCs keep increasing as new EPCs are nucleated. As the number of EPCs reaches the peak value, it is envisioned that the EPC coalescence would become dominant.

According to the nuclear magnetic resonance (NMR) measurements as well as the atomistic simulations [13-15], there is an interface zone of the thickness of a few nanometers in a nanopore, as depicted in Fig. 1. For mesoporous or macroporous materials, the pore size is larger than the characteristic interface-zone thickness. In order to analyze the average flow rate of confined liquid  $\overline{\nu}$ , both the contributions of the interface flow and the normal flow in the interior must be taken into consideration [10,16]. For a microporous material, however, the pore size can be smaller than the thickness of interface zone and, therefore, the normal flow is negligible. Under this condition, the effective flow rate is dependent on the applied pressure p, the effective kinematics viscosity of confined liquid  $\chi$ , the pore size r, as well as  $\gamma$ . Note that the molecular density in the interface zone is a function of  $\gamma$  [17]. According to the  $\Pi$  theorem, by assuming that the  $\overline{v}$ -p relationship can be described by a power-law equation, the average flow rate can be stated as

$$\frac{\gamma \overline{v}}{\chi p} = \alpha \left(\frac{pr}{\gamma}\right)^{\beta} \tag{1}$$

where  $\alpha$  and  $\beta$  are system parameters. The form of Eq. (1) is compatible with the experimental observation that the average diffusion rates of confined liquids in nanoporous materials follow power-law functions [13,14]. For normal flow,  $\beta$ =1; for subdiffusive flow,  $\beta$ <1; and if  $\beta$ >1, the flow is of a superdiffusive characteristic.

An EPC consists of a number of empty pores connected together and can be characterized by its radial depth c and the circumferential width l, as shown in Fig. 2. The collective EPCs can be characterized by the number density n(c,l,t), which is defined as the number of EPCs of size  $\{c,l\}$  at time t. Following the classic number density equilibrium equation, the evolution of n(c,l,t) is governed by

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Fig. 1 Schematic diagram of the confined liquid in a nanopore

$$\frac{\partial n(c,l,t)}{\partial t} + \frac{\partial}{\partial c} [C(c,l,t)n(c,l,t)] + \frac{\partial}{\partial l} [L(c,l,t)n(c,l,t)] = n_N(c,l,t)$$
(2)

where *C* and *L* are the EPC growth rates along the radial and circumferential directions, respectively; and  $n_N$  is the nucleation/coalescence rate. Equation (2) describes the mass transportation between the EPCs to the saturated area.

As a first-order approximation, C and L can be taken as the average growth rate of the EPC-FPC boundary

$$C = L = \tilde{\alpha} \int_{0}^{\infty} P(r)\bar{v} \, \mathrm{d}r \tag{3}$$

where P(r) is the pore size distribution, which can be considered as a lognormal function with the mean value of  $\overline{r}$  and the standard deviation of  $\sigma_r$ ; and  $\tilde{\alpha}$  is a parameter accounting for the orientational correlation of the micropores. For isotropic porous structure, the directions of confined flows in nanopores are random, and therefore  $\tilde{\alpha}=2/3$ .

The term of  $n_N$  consists of two components

$$n_N(c,l,t) = \tilde{n}_N(c,l,t) + n_C(c,l,t) \tag{4}$$

where  $\tilde{n}_N$  is caused by EPC nucleation and  $n_C$  is the component associated with EPC coalescence. The nucleation rate can be stated as

$$\widetilde{n}_N(c,l,t) = \eta_0 P(c \leqslant r_0) \left[ 1 - \frac{V(t)}{\left(\frac{4}{3}\right)\pi R^3} \right]_{c=1}$$
(5)

where  $r_0 = 2\gamma/p$ , *R* is the particle radius,

$$V(t) = \varsigma \int \int_{c,l} n(c,l,t) c l^2 dc dl$$
(6)

is the total volume of EPCs, and  $\eta_0 = \eta_1 \int_{-0}^{r_0} P(r) dr$ , with  $\zeta$  being a geometry factor and  $\eta_1$  a parameter determined by the time reso-



Fig. 2 Schematic diagram of a microporous particle

lution. For regular-shaped EPCs,  $\zeta = 1$ . The term in the brackets in Eq. (5) is the volume fraction of FPCs.

If the distribution of the EPC nucleation sites is random, the EPC coalescence can be analyzed in the framework of conditional probability theory [18]

$$p_{\rm d} R/d = \sqrt{N_{\rm d}} (R/1 - d)^{\sqrt{N_d} - 1}$$
 (7)

where  $p_d$  is the probability for two adjacent EPCs to be *d* apart and  $N_d$  is the total number of the EPCs in the area under consideration. When the sum of the radial depths of two EPCs equals the distance between them, the radial coalescence occurs and the associated probability is

$$f_R(d,t) = \eta p_d(R/d) \int_0^d n_c(c,t) \int_0^{d-c} n_c(\tilde{c},t) d\tilde{c} dc$$
(8)

where  $n_c(c,t) = \int_0^\infty n(c,l,t) dl$ ,  $\eta \propto 1/N^2$  is a normalization constant, and  $N_d$  can be expressed as  $M(V/N)^{2/3}R J/\frac{4}{3}\pi R^3$ , with  $N = \int \int_{c,l} n(c,l,t) dc dl$  being the total EPC number.

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The lateral coalescence, on the other hand, is dependent on the distance of the EPCs to the center of the particle r. The probability of the coalescence along the circumferential direction of two EPCs that are initially d apart is

$$f_L(r,d,t) = \eta' \cdot p_{\mathrm{d}}(2\pi r/d) \int_0^d n_L(l,t) \int_0^{d-l} n_L(\tilde{l},t) \mathrm{d}\tilde{l}\mathrm{d}l \qquad (9)$$

where  $n_L(l,t) = \int_0^\infty n(c,l,t) dc$  and  $\eta' \propto 1/N^2$  is a normalization constant. In Eq. (9), the effective EPC number  $N_d$  should be taken as  $3Nr^2(V/N)^{1/3}/R^3$ .

Consequently, the contribution of EPC coalescence is

$$n_{c}(c,l,t) = n_{cR}(c,l,t) + n_{cL}(c,l,t)$$
(10)

The two terms at right-hand side of Eq. (10) capture the effects of radial and lateral coalescences, respectively, and

$$n_{ci}(c,l,t) = N(t) [\tilde{p}_i(c,l,t) - 2\hat{p}_i(c,l,t)]$$
(11)

where  $\tilde{p}_i$  reflects the contribution of EPC formation,  $\hat{p}_i$  reflects the contribution of EPC disappearance, and the subscript i=R or L denotes the radial or lateral direction, respectively. These components can be stated as

$$\widetilde{p}_{R}(c,l,t) = n_{L}(l,t) \int_{0}^{R} f_{R}(d,t) \Biggl\{ \int_{0}^{R-d} n_{c}(\widetilde{c},t) \int_{0}^{R-d-\widetilde{c}} n_{c}(\widehat{c},t) \mathrm{d}\widehat{c} \mathrm{d}\widetilde{c} \Biggr\} \mathrm{d}d$$
(12*a*)

$$\widetilde{p}_{L}(c,l,t) = n_{c}(c,t) \cdot \int_{0}^{R} \int_{0}^{r} f_{L}(r,d,t)$$

$$\times \left\{ \int_{0}^{2\pi r-d} n_{L}(\tilde{l},t) \int_{0}^{2\pi r-d-\tilde{l}} n_{L}(\hat{l},t) d\hat{l} d\hat{l} \right\} dddr$$
(12b)

$$\hat{p}_{R}(c,l,t) = n_{L}(l,t) \cdot \int_{0}^{R} f_{R}(d,t) \left[ \int_{0}^{R-d} n_{c}(\tilde{c},t) \mathrm{d}\tilde{c} \middle/ n_{c}(c \leq R) \right] \mathrm{d}d$$
(12c)

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Fig. 3 Evolution of the number density of EPCs

$$\hat{p}_{L}(c,l,t) = n_{c}(c,t) \cdot \int_{0}^{R} \int_{0}^{r} f_{L}(d,t)$$

$$\times \left[ \int_{0}^{2\pi r - d} n_{L}(\tilde{l},t) \mathrm{d}\tilde{l} \middle/ n_{L}(c \leq 2\pi r) \right] \mathrm{d}d\mathrm{d}r$$
(12d)

Finally, the model is completed by setting the initial condition as n(c,l,0)=0, that is, initially the particle is fully saturated; and setting the boundary condition as n(0,0,t)=0.

#### **3** Results and Discussion

Figure 3 shows the numerical results of Eqs. (3)-(12), where the average pore size  $\overline{r}=1$  nm,  $\sigma_r=0.3$  nm,  $\gamma$  is taken as 20 mJ/m<sup>2</sup>,  $p=2.0 \times 10^4$  Pa, and  $\beta \approx 1.3$ . The value of  $\nu$  is set to  $3.2 \times 10^{-6}$  m<sup>2</sup>/s. It can be seen clearly that the  $n_c(c,t)$  distribution consists of two regions separated by an abrupt drop in  $n_c$ . A similar characteristic can also be observed in the  $n_{\rm L}(l,t)$  distribution curves. The boundary of the two regions is close to  $\int_0^t C dt$ , which would be the upper limit of the EPC size at time t if the EPC coalescence did not occur. The lower c region is dependent on the EPC nucleation, growth, and coalescence, while the higher c region is mostly determined by the coalescence behavior, particularly, the term of  $\hat{p}_i$  in Eq. (11). The coalescence leads to the tendency of decrease in  $n_c$  in the lower c region and the increase in the higher c region. As the average size and volume fraction of EPCs increase, the coalescence becomes increasingly important and the higher c region dominates the system behavior. The height of the abrupt drop between the two regions keeps decreasing and eventually vanishes. When the effective dewetting process is completed,  $n_c$  in the lower c region is reduced to zero and there is only one EPC left in the higher c region with the size of R.

The evolution of the average EPC size  $\overline{c}$  is highly nonlinear, as shown in Fig. 4. In the early stage of dewetting, before the EPC coalescence becomes pronounced, the increase in  $\overline{c}$  is mostly caused by the EPC growth, which is quite slow. As  $t/t_{dw}$  reaches 0.5,  $\overline{c}$  is only about 1% of *R*, with  $t_{dw}$  being the dewetting time. After that, with the increasing EPC volume fraction the coalescence leads to the rapid increase in  $\overline{c}$  as small EPCs merge together. Compared to that of  $\overline{c}$ , the extent of nonlinearity of the evolution of EPC volume fraction is much lower, since EPC coalescence cannot be reflected in the *V*-*t* relation. As *V* rises, because of the reduction in the number of available nucleation sites, the nucleation rate is lowered, which reduces dV/dt. Furthermore, the coalescence causes a decrease in the specific area of the EPC-FPC interface, which retards the EPC growth. As a result, V(t)increases with a descending rate.



Fig. 4 Evolution of the average size and the total volume fraction of EPCs

In a number of engineering applications, the nanoporous materials work under dynamic environments with the pressure differences varying in broad ranges. The rate of pressure change  $\dot{p}$ affects  $t_{dw}$  by influencing  $\overline{v}$  (see Fig. 5). The characteristic time  $t_0$ is taken as the dewetting time if the pressure were fixed at the initial value. As  $\dot{p}$  increases, with everything else the same,  $\bar{v}$  is higher and thus  $t_{dw}$  is lowered. Note that increasing the average pore size  $\overline{r}$  and decreasing the dewetting "driving force"  $\gamma$  have similar effects. The dewetting time is also a function of  $\beta$ . When  $\beta=1$ , the flow rate in the nanoenvironment is proportional to r, and Eq. (2) is reduced to that of normal flow. If  $\beta < 1$ , subdiffusive process dominates and the dewetting takes a longer time, and vice versa. It is clear that with a constant  $\overline{r}$ , the broader the poresize distribution, the more large pores are involved in the EPC growth. Because  $\overline{v}$  increases with r, although as  $\sigma_r$  rises the fraction of small pores becomes higher, the overall effect of raising  $\sigma_r$ is beneficial to reducing  $t_{dw}$ . However, since changing  $\sigma_r$  does not directly affect the EPC coalescence, and the influence of EPC growth is important only in the early stage, the  $\sigma_r$  dependence of  $t_{\rm dw}$  is relatively weak.

#### 4 Conclusion

A pore-cluster model is developed so as to provide an appropriate framework for the study on the aggregate behaviors of



Fig. 5 Dewetting time as a function of  $\dot{p}\bar{r}/\gamma$  and  $\beta$ 

nanoporous systems. Although the details of the solid-liquid interaction and the EPC geometry are not taken into consideration and currently it is difficult to directly compare the theoretical results to experimental data, the system response (e.g., the dewetting time) can be related to the control parameters quite conveniently by the EPC number density analysis. The numerical results indicate that there exist two abruptly separated regions in the EPC number density distribution, with the lower c region formed by the EPC nucleation and the higher c region dominated by the EPC coalescence. At the early stage of dewetting, the EPC nucleation is the most important factor affecting n, whereas at the late stage the EPC coalescence results in the eventual disappearance of the lower c region and the rapid increase in average EPC size. The dewetting time decreases as the mean value or the standard deviation of pore-size distribution increases.

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