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Molecular Modeling of Mercury Porosimetry

F. PORCHERON AND P.A. MONSON*
Department of Chemical Engineering, University of Massachusetts, Amherst 01003, MA, USA
monson@ecs.umass.edu

M. THOMMES
Quantachrome Instruments, Boynton Beach, FL, USA

Abstract. We present a molecular thermodynamic approach to model mercury porosimetry. A lattice model is used to describe the intrusion/extrusion of mercury into different pore structures. The non-wetting nature of mercury is modeled by setting the wall-fluid interaction of the lattice model to repulsive values. We perform Mean-Field Density Functional Theory calculations on a mesoporous Vycor glass for different temperatures. The shape of the intrusion/extrusion curves is in good agreement with experimental observations. Visualizations of the liquid distribution in the Vycor glass reveal a fragmentation of mercury along the extrusion curve. The calculations performed on ink-bottle pore show that this fragmentation is caused by the snap-off of mercury from the necks leading to a droplet of mercury entrapped into the bottle part of the pore. This phenomenon is likely to play a role in the mechanism of mercury entrapment frequently observed during experiments.

Keywords: mercury porosimetry, lattice model, Vycor

1. Introduction

The characterization of porous materials is very important for applications in areas like catalysis, separations and gas storage. Experimentally the void structure of a material is often investigated by performing gas adsorption/desorption isotherms in which the adsorbing gas (usually nitrogen) wets the interior surfaces of the porous material (Everett, 1967). A complementary technique is mercury porosimetry. The principle, originating from Washburn, is to force a non-wetting liquid (mercury) to penetrate into the porous structure of the material. The hydraulic pressure P_h imposed is many times greater than the saturation vapor pressure P_0 and one refers to intrusion/extrusion of the mercury into the material rather than adsorption/desorption for gas adsorption experiments. Mercury intrusion into a porous network is often described using the Washburn equation:

$$P_h = \frac{-2\gamma \cos\theta}{r} \tag{1}$$

where γ is the surface tension, θ the contact angle and r the pore radius. Following this equation, the hydraulic pressure required for intrusion increases when the pore radius decreases. The technique is most useful to investigate pores of mesoscopic sizes (>10 nm). During an experiment a cycle of intrusion and extrusion is performed and several features are usually observed (Leon y Leon, 1998; Lowell and Shields, 1991; Van Brakel et al., 1981). The pressure required for the mercury to enter the pore structure is very high and depending on the materials one might reach the upper pressure limit of the porosimeter before the mercury has filled all the pores of the material. A hysteresis is always observed between the intrusion and the extrusion branch. Quite often at the end of a cycle, the extrusion branch does not close the intrusion branch revealing that some mercury

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*To whom correspondence should be addressed.

has been entrapped into the material. This quantity can reach up to 90% of the mercury volume intruded at high pressure.

Compared to gas adsorption (Evans, 1992; Gubbins, 1997) the modeling of mercury porosimetry experiments has received less attention. Moreover most of these works rely on a percolation network approach rather than molecular models (Matthews et al., 1995; Rigby, 2000; Rigby et al., 2001, 2002). Recently a lattice model has been successfully used to describe gas adsorption in mesoporous materials (Kierlik et al., 2001; Woo and Monson, 2003; Sarkisov and Monson, 2002; Woo et al., 2001, 2004). In a recent paper (Porcheron et al., 2004), we showed that this model also offers a useful molecular approach to modeling mercury porosimetry. In this paper we review this approach and provide some additional calculations which illustrate the approach using Mean-Field Density Functional Theory (MF-DFT). The remaining of the paper will be organized as follows. Section 2 is devoted to the description of the models and method used in this work. We then present the results obtained in Section 3 and finally some conclusions and perspectives presented in Section 4.

2. Models and Methods

2.1. *Lattice Model*

In the lattice model, the space is discretized into sites using a simple cubic lattice. Each of these sites can either be occupied by a solid particle or available for the presence of fluid. We only consider the nearest-neighbors interaction and the Hamiltonian of the system then takes the simple form:

$$\begin{aligned} H = -\varepsilon \sum_{i,j} n_i n_j t_i t_j - \mu \sum_i n_i t_i \\ -\alpha\varepsilon \sum_{i,j} [n_i t_i (1 - t_j) + n_j t_j (1 - t_i)] \end{aligned} \tag{2}$$

where n_i(=0 or 1) is the fluid occupation variable and t_i is the solid occupation variable representing whether the site is occupied by a solid particle ($t_i = 0$) or available for fluid occupation ($t_i = 1$). ε is the fluid-fluid interaction parameter, μ is the chemical potential and α is the wall-fluid interaction parameter. The sums run over all the distinct pairs of nearest neighbor sites.

2.2. *Mean-Field Density Functional Theory*

Mean-Field Density Functional theory starts with the expression of the grand potential Ω of the model:

$$\begin{aligned} \beta\Omega = \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] - \beta\mu \sum_i \rho_i \\ - \beta\varepsilon \sum_{i,j} \rho_i \rho_j - \beta\alpha\varepsilon \sum_{i,j} [\rho_i t_j + \rho_j t_i] \end{aligned} \tag{3}$$

where $\beta = 1/kT$ where k is Boltzmann's constant, ρ_i is the local density at site i, and μ is the chemical potential. Minimization of Ω with respect to the local densities ρ_i yields the following set of nonlinear algebraic equations:

$$\rho_i = \left\{ 1 + \exp\left[\beta \left\{ -\mu - \varepsilon \sum_{j \in i} [\rho_j + \alpha(1 - t_j)] \right\} \right] \right\}^{-1} \tag{4}$$

These equations are solved numerically by iteration starting from an initial estimate. The average fluid density across the system is then given by averaging the local density ρ_i. The intrusion/extrusion isotherms are obtained as follows. We proceed by starting from an empty material at low μ and increasing the chemical potential until the average density corresponds to an almost completely filled structure. Then we decrease μ in a sequential process to obtain the extrusion branch.

2.3. *Pore Models*

In this work we consider two different pore structures for the lattice model. The first one is a mesoporous Vycor glass obtained *via* the Gaussian random field method described elsewhere (Woo and Monson, 2003). This method allows the generation of realistic samples of the Vycor glass consistent with the experimental structure factor obtained from neutron scattering experiments. A configuration of the Vycor glass obtained with this method is represented in Fig. 1.

The porosity of the Vycor is 30% and we ensure that the void structure displays bicontinuity. The dimension of the sample in each direction is 180 lattice sites and

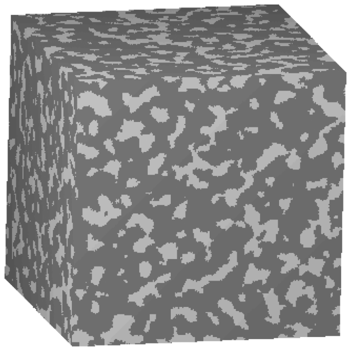

Figure 1. Snapshot of the Vycor sample used in this work. The light parts represent the porous network whereas the dark parts represent the solid structure. The dimension of the Vycor is 180 lattice sites in each spatial direction.

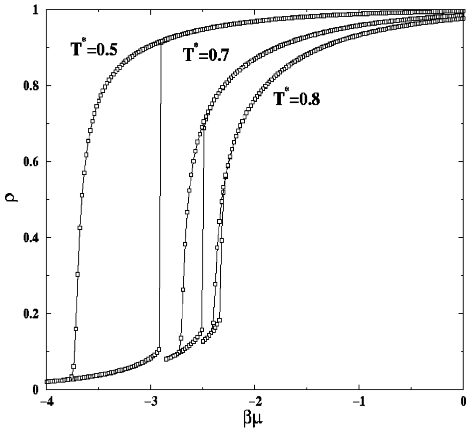

Figure 2. Intrusion/extrusion isotherms into a mesoporous Vycor glass obtained by MF-DFT for different temperatures ($T^* = T/T_c = 0.5, 0.7, 0.8$) and $\alpha = 0$.

the lattice parameter is set to $a = 15$ Å, corresponding to a linear sample size of 270 nm.

The second structure is a slit pore version of the ink-bottle geometry where a wide slit pore (bottle) is connected to a smaller one (necks) at its extremities (Sarkisov and Monson, 2001). Each of these necks is then connected to a bulk reservoir. In this work, we set the widths of the bottle and the necks to 12 and 6 lattice sites respectively.

3. Results

To model the non-wetting nature of the mercury we set the α parameter to values $\alpha < 1/2$ which represent a repulsive wall-fluid interaction in the lattice Hamiltonian. We first perform a series of calculations on a mesoporous Vycor glass for different temperatures and $\alpha = 0$. The corresponding intrusion/extrusion isotherms are represented in Fig. 2.

Clearly the isotherms display a hysteresis for each studied temperature and the width of this hysteresis decreases with increasing temperature. The pressure required for the intrusion of the mercury into the Vycor is above the bulk saturation chemical potential which means that bulk mercury in contact with the Vycor would be in a liquid state as expected. The intrusion isotherm in the hysteresis domain is very sharp and the mercury penetrates the Vycor over a very small range of μ. In contrast, the extrusion process spreads over a larger range of chemical potential.

Inspection of the snapshots (see Fig. 3) during the intrusion process reveals that the mercury preferentially penetrates into the larger pores as qualitatively predicted by the Washburn equation. Then at higher pressures the pores of smallest dimensions and the fluid sites located close to wall sites are filled. The retraction of the mercury starts with the voidage of near-wall sites and then progress in a fragmented way over the whole material. A further observation of the snapshots indeed reveals that the mercury is highly fragmented even for the late stages of the extrusion where the pressure is

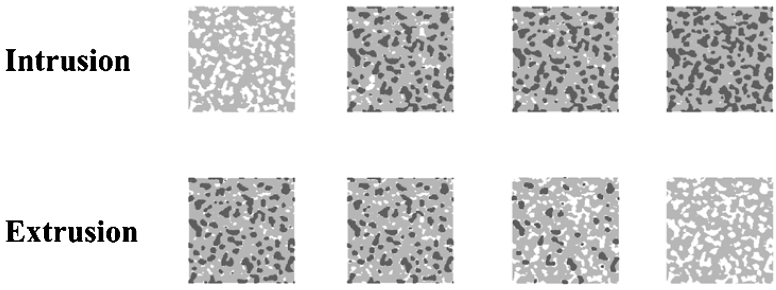

Figure 3. Representative snapshots of the mercury intrusion/extrusion cycle into the mesoporous Vycor glass.

Figure 4. Representative snapshot of a mercury droplet entrapped into the ink-bottle pore during the extrusion process. $T^* = 0.7$, $\alpha = -1$.

close to P_0. It seems likely to us that this fragmentation process is related to the mercury entrapment often observed in the experiments.

To further understand this behavior we perform a series of calculations on an ink-bottle pore in contact with bulk reservoirs. We find that during the extrusion process, under certain conditions the mercury might snap-off from the necks leading to a residual droplet into the bottle part of the pore (see Fig. 4). In a realistic picture, the only way for this droplet to extrude from the pore is *via* vapor diffusion through the neck part of the pore. Therefore the extrusion path for droplets entrapped deeply within the Vycor glass is complex and extremely slow. This kinetic problem is confirmed by experimental observations which mention that the mercury can sometimes continue to extrude for hours at the completion of an intrusion/extrusion cycle (Lowell and Shields, 1991).

4. Conclusions

In conclusion, we have modeled mercury porosimetry within the framework of a lattice model. The non-wetting nature of the mercury is accounted for by setting the wall-fluid interaction parameter to repulsive values ($\alpha < 1/2$). Intrusion/extrusion isotherms obtained on a realistic sample of a mesoporous Vycor glass displays several features observed in experiments. Although our model did not capture the entrapment at the end of an extrusion branch, we believe that it appears as a consequence of highly fragmented mercury in the vicinity of ink-bottle pore in agreement with previous observations (Matthews et al., 1995). The reason why entrapment is observed may be more related to a dynamic issue and therefore suited to Kawasaki dynamics simulations. Work is in progress to further illustrate this aspect.

Finally, we mention that the lattice model can be used to understand the relationship between gas adsorption and mercury porosimetry experiments. The lattice gas model we are using exhibits a symmetry with respect to $\alpha = 1/2$ and $\rho = 1/2$ and $\mu = \mu_0$ (Porcheron et al., 2004). This leads to a relation between the vapor pressure (P/P_0) and the hydraulic pressure (P_h) used as control parameters in gas adsorption and mercury porosimetry experiments respectively. Such relationships have been proposed in previous work in analyzing experimental data (Murray et al., 1999; Lowell and Shields, 1981).

Acknowledgments

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