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Improving structural analysis of disordered mesoporous materials using NMR cryoporometry

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ABSTRACT

A microscopic, lattice-fluid model was employed to analyze freezing and melting behavior of fluids confined to linear pores of mesoporous silicon. The model predicts that mesoscalic disorder, inherent to this material, results in strong pore-blocking on freezing. On the other hand, it reveals that the existence of disorder leads to an interplay of three different mechanisms controlling the melting behavior. They are shown to be associated with metastable radial melting of pore narrowings, with axial melting of superheated solid, and with inverse pore-blocking due to the largest pores. On the basis of these findings, strategies for the improvement of structural analysis of mesoporous solids using cryoporometry techniques are discussed.

1. Introduction

Thermo- or cryoporometry is a method of structural analysis based on measurements of the solid–liquid phase transition temperatures for fluids confined to mesoporous solids. This temperature is generally known to be altered by the confinements as compared to the equilibrium transition temperature T_0 of the bulk liquid. By interrelating the difference between these two temperatures to the pore size, the latter can be estimated in a way similar to approaches used for structural analysis using gas sorption measurements, in which the suppression of the condensation or evaporation pressures is probed [1]. In thermoporometry, detection of the transition temperature is most commonly based on the measurement of the amount of heat released or consumed during the transition using differential scanning calorimetry [2,3]. Alternatively, application of advanced experimental techniques such as X-ray scattering [4,5], ultrasonic attenuation measurements [6] or nuclear magnetic resonance cryoporometry [7,8] have been proven to provide more direct information on the fluid state and phase composition in porous materials. However, incomplete understanding of some fundamental questions concerning solid–liquid equilibria in confined spaces renders quantitative structural analysis using all these techniques relatively approximate.

The primary goal of cryoporometry is to assess the pore size distribution function (PDF) for a given porous solid. It is typically done by probing the relative amount of liquid (or frozen) phase in the pores as a function of temperature upon warming the system from the completely frozen state, attained at sufficiently low temperatures (the freezing branch is rarely used due to uncontrollable nucleation delays). To convert this function, in what follows referred to as melting curve, to PDF, the pore system is approached by a collection of cylindrical pores with different diameters. It is further assumed that melting in each pore occurs independently from others and the melting temperature T_m in the channel is solely determined by its diameter d. Different macroscopic models developed for materials with ideal pore geometries, e.g. cylinders or slits, lead, as a first approximation, to the Gibbs–Thomson-type equation $\Delta T = K/d$, which relates the suppression ΔT of the transition temperature to d. With known thermodynamical parameters for the liquid used, the cryoporometry constant K can be calculated within the theory. Alternatively, K can be calibrated by measuring ΔT for a set of porous materials with known structural characteristics. With the Gibbs–Thomson equation, the (volume) fraction of pores having certain pore size is readily determined [9,10].

Often, however, pore spaces in porous materials are far from having ideal pore geometries. Network and, especially, disorder effects may alter the freezing and melting behavior appreciably. As an example, the pore-blocking phenomenon is known to give rise to strong metastabilities on cooling [11,12]. Their effect on the melting behavior is less obvious, although exactly this transition is typically used for determining structural properties of porous solids. It is worth mentioning, in this respect, that we have noted that NMR cryoporometry systematically delivers smaller pore sizes for mesoporous silicon as compared to the data obtained using more conventional scanning electron microscopy or advanced gas sorption methods [13,14]. Notably, this material, which can be prepared to have tubular pores [15–18], was shown to possess substantial

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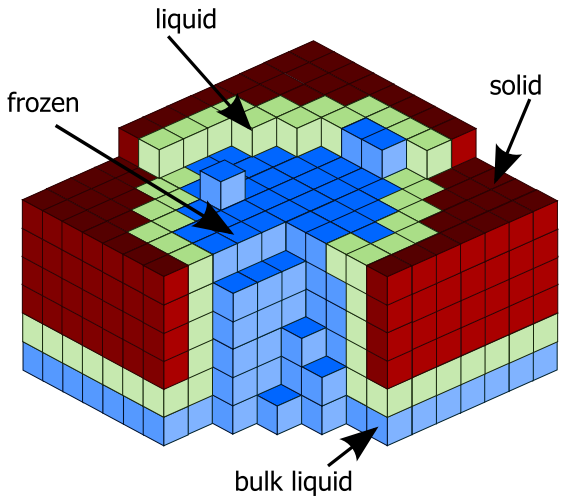

Fig. 1. A cut-off of the simulation box showing a cylindrically-shaped pore containing the lattice sites forming the frozen core in the pore ('frozen' sites) and non-frozen surface layer ('liquid' sites). At the pore opening (bottom) , contact to the frozen bulk liquid is provided.

disorder, namely variation of the average pore diameter along the pore axis and some finite atomistic disorder [18,19]. In this respect, it can be considered as a most suitable experimental system with one-dimensional pore space organization to study disorder effects, without further complications existing in networked materials.

To get deeper insight into the discrepancies, often found between the data of different methods of structural analysis as applied to mesoporous silicon, the disorder inherent to the pore space organization in this material has to be incorporated into the analysis of the experimental data delivered by NMR cryoporometry. Most unambiguously, it can be done using molecular dynamics simulation studies [20,21]. Alternatively, a microscopic theory, analogous to lattice-gas models used for the analysis of gas–liquid equilibria under confinement, can be formulated and solved in, e.g. mean field theory or using computer simulations [22]. Clearly, some fine details, such as molecular shape or interaction anisotropy, cannot be included if the second option is followed. However, most essential details required to understand qualitatively the effects of disorder upon fluid behavior are well captured. In this work, we present such a microscopic lattice-fluid model, which will apply to analyze melting behavior of fluids in disordered channels of mesoporous silicon.

2. Microscopic model

To study freezing and melting behavior in disordered porous materials, we have used a lattice-site Kossel–Stranski model which has initially been developed to study crystal growth processes in bulk systems [23]. In this model, the frozen (crystalline) phase is considered as a crystal which is composed of cubic molecules. The binding of a molecule to the crystal depends on its neighbors. Even this simple approach has been proven to contain most essential ingredients to explain many features of bulk crystal growth processes, including crystal shape anisotropy and the existence of the roughening transition.

The approach can easily be extended to address solid–liquid equilibria in porous media as described in what follows. In our model (see Fig. 1), fluid molecules are modeled as lattice sites, which may exist in two states, 'frozen' and 'liquid' ones. The lattice sites are surrounded by the pore walls, which are modeled in a similar way as the lattice sites in the 'solid' state. The sites interact with each other and the interaction energy depends on the state of the two interacting sites. Let us denote the bond energy between two 'frozen' sites by ϵ and the absolute value of the bond energy between the 'frozen' and 'solid' sites by ϕ. ϵ can be related to the latent heat of transformation L. Indeed, the latter can be considered as the total binding energy per molecule in the 'frozen' state if it is surrounded by the sites in the 'frozen' state. Because each bond is shared between two 'frozen' sites, the total binding energy per site is $z\epsilon/2$, where z is the number of nearest-neighbor sites. Thus, for the cubic symmetry considered in this work, $L = 3\epsilon$. The difference ΔG in the free energy (per site) upon converting a site which is initially in the 'liquid' state into the 'frozen' state is

$$\Delta G = -n\epsilon + T\Delta S + N\phi, \tag{1}$$

where n and N are the numbers of neighbor sites in the 'frozen' and 'solid' states, respectively, T is the current temperature, and ΔS is the entropy change associated with adding the 'frozen' site to the crystal. At the bulk equilibrium transition temperature, T_0, the latent heat is compensated by the entropy change. Thus, ΔS in Eq. 1 can be replaced by L/T_0.

Most straightforwardly, the problem can be considered using Monte Carlo simulations. First, the 'solid' sites have to be arranged in the simulation box to model the porous solid framework. In this work, we have considered liquids completely wetting the pore walls. This was done by taking the interaction energy ϕ to be equal to 10ϵ. Notably, variation of ϕ (keeping $\phi > \epsilon$) has an only quantitative effect and does not change the qualitative conclusions obtained with $\phi = 10\epsilon$. During simulations, the probability to change the state of a randomly chosen fluid site has been found according to the Metropolis rule based on the energy change according to Eq. 1 [24].

3. Simulation results and discussion

The main purpose of this work was to perform computer experiments of cryoporometry with linear, disordered pores mimicking channels in mesoporous silicon. To verify the applicability of the theoretical model described in the preceding section, however, we have first applied it to porous materials with nearly (owing to lattice-site model) ideal cylindrical pores. In the simulations, the site length was taken equal to 0.5 nm, L was set equal to 10 kJ/mol. The channels were open at both ends. Bulk liquid was supplied at the pore openings. The equilibrium transition temperature T_0 was fixed to 278.9 K and the kinetic nucleation delay in the bulk phase was intentionally removed. During simulations, the temperature was changed stepwise and, after given a sufficient

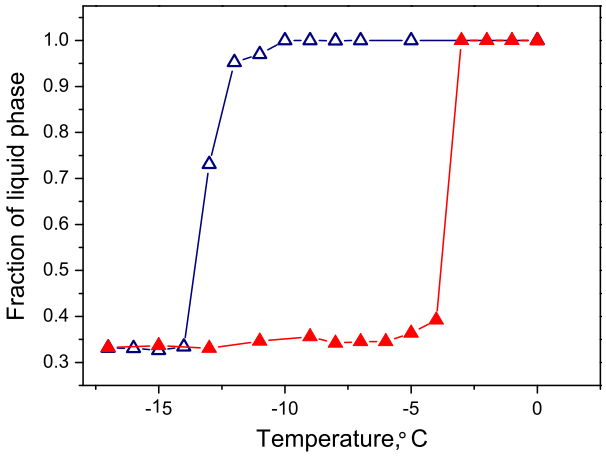

Fig. 2. The relative fraction of liquid phase as a function of temperature in ideal cylindrical pores with the channel diameter of $d = 6$ nm open at both ends as measured upon cooling (open symbols) and warming (filled symbols).