Thermodynamics of confined nano-phases ☆

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ABSTRACT

We consider a phase of nano-scale dimensions (the adsorbate) confined within a porous material, and in thermal, chemical and mechanical equilibrium with a bulk phase of fixed temperature, pressure and composition. From a corresponding states analysis of the partition function for pores of simple geometry (e.g., slit- or cylinder-shaped) we show that the principal system variables for most cases are the pore shape and width (expressed in terms of molecular diameters), H^*, and a microscopic wetting parameter, α_w, that is a measure of the relative strength of the adsorbate-wall and adsorbate–adsorbate interactions. We illustrate the utility of this model by considering experimental, theoretical and molecular simulation results for adsorption, (vapor + liquid) condensation for pure fluids and mixtures, freezing, and pressures for these confined nano-phases. The wetting parameter is shown to be of central importance, determining both the magnitude of the effects of confinement and also the qualitative behavior, for example, whether the freezing temperature is raised or lowered upon confinement. These confinement effects become larger as the pore width is reduced; reducing the pore width can also result in qualitative changes, such as phase changes. For pores of slit- or cylinder-shape there are two independent pressures within the pores, one acting normal to the pore walls and one (the tangential pressure) acting parallel to the walls. Molecular simulation results show that these two pressures, which are of the order thousands or tens of thousands of bars for small pores in equilibrium with a bulk phase at ambient pressure, differ greatly in magnitude and in their response to changes in the system and state variables.

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1. Introduction

Fluid or solid phases of nano-scale dimensions, when in contact with a solid surface or confined within a narrow pore, such as occurs in a nano-porous solid (e.g., carbons and oxides of various kinds), within a living cell, reverse micelle, or clathrate hydrate, have thermodynamic properties that are often very different from those of the macroscopic bulk material. These confinement effects arise because of reduced dimensionality and strong interaction of the molecules in the nano-phase with the confining walls. Examples of such effects are shifts in phase boundaries, the presence of new surface-driven phases, heats of adsorption, enhanced pressures, selective adsorption in the case of mixtures, and shifts in chemical equilibrium for reactions. In addition to these effects on thermodynamic properties, some familiar thermodynamic laws and concepts can break down at the nano-scale. These include Gibbs surface thermodynamics, including the concept of surface tension (for sufficiently small nano-phases there is no well-defined surface separating two bulk phases) and laws based on these concepts that include Kelvin, Laplace, Young, Gibbs–Thomson and similar equations. Similarly, the Second Law of Thermodynamics breaks down at the nano-scale, due to the increasingly large fluctuations that occur as system size is decreased. As noted by Maxwell in his review of Tait's book on thermodynamics [1]:

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Hence the Second Law of Thermodynamics is continually being vio-lated and that to a considerable extent in any sufficiently small group of molecules belonging to any real body.

In such nano-scale systems the Second Law is replaced by a fluctuation theorem that applies to small systems for short periods of time [2,3]. The fluctuation theorem leads to the Second Law in the thermodynamic limit ($N \to \infty$, $\rho = N/V$ = constant, where N and V are the number of molecules and volume).

A further complication in nano-scale systems is that some familiar properties may not be uniquely defined. Examples are the volume and the pressure. In the case of a confined nano-phase, we must make a choice of where to draw the system boundaries. For example, we might define the boundary as the surface drawn through the centers of the atoms on the wall's surface (a suitable choice for neutron scattering studies) or a surface that excludes some dead volume near the walls (often used in adsorption stud-ies). For properties such as volume and pressure, we must make an operational definition [4].

Theory, including molecular simulation, and experiment have different strengths and limitations, and are to a large extent complementary in this area. Significant difficulties in experimen-tal studies of confined nano-phases include measurement of the composition and structure of the confined phase, long-lived metastable states, preferential adsorption of trace components, and measurement of many properties of the confined phase, *e.g.*, pressures. Difficulties in theoretical and simulation studies include uncertainty about the detailed atomic structure of the confining medium (*e.g.*, pore morphology and topology in the case of porous materials), and about the force fields involved. Moreover, for large and flexible molecules or particles, such as polymers, proteins and colloids, insufficient computer power remains a limitation. This latter difficulty should be ameliorated in the next few years, when Exo-flop and faster supercomputers become available.

In this paper, we give an overview of the current state of knowl-edge of some of the main confinement effects on the thermody-namic behavior of nano-phases. In Section 2, we consider the conditions of equilibrium for the confined phase, and the principal variables that influence confinement effects. In Section 3, we dis-cuss two examples of such effects: the effect of confinement on phase changes within the pores, and on the in-pore pressures.

2. Thermodynamics of confined phases

2.1. Condition of phase equilibrium

We consider a porous material (or other confining medium) that reaches equilibrium with a bulk phase, usually a gas or liquid, as shown schematically in figure 1. At equilibrium, the conditions are:

$$
\begin{aligned}
\mu_{\text{bulk}} &= \mu_{\text{confined}}, \\
T_{\text{bulk}} &= T_{\text{confined}}, \\
\nabla \cdot \mathbf{P} &= -\rho(\mathbf{r}) \nabla \upsilon(\mathbf{r}),
\end{aligned}
\tag{1}
$$

where μ is chemical potential, T is temperature, $\mathbf{P}$ is the pressure tensor, and $\rho(\mathbf{r})$ and $\upsilon(\mathbf{r})$ are the number density and the external field acting at point $\mathbf{r}$. Subscripts *bulk* and *confined* indicate values for the bulk and pore phases, respectively.

The first two of these equations are the familiar conditions of thermodynamic equilibrium for bulk phases. We note that although the density and pressure vary rapidly with the position within the pore, the chemical potential is everywhere constant. The third equation is the condition of mechanical, or hydrody-namic equilibrium, and is the generalization to inhomogeneous
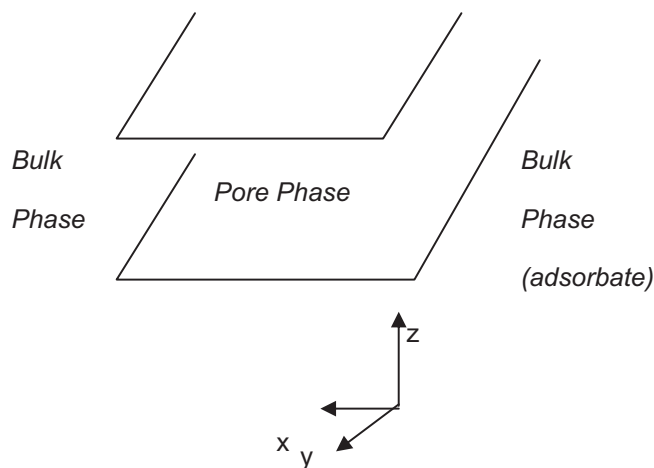

FIGURE 1. Equilibrium between a bulk phase and the pore phase.

phases of the usual hydrodynamic condition for bulk homoge-neous phases. It arises from the requirement that there be no net momentum flow between the two phases at equilibrium (see reference [4], Section 8.3). In the applications considered here, there is no external field and so the hydrodynamic equilibrium condition becomes:

$$
\nabla \cdot \mathbf{P} = 0.
\tag{2}
$$

The pressure within the pore is a second-order tensor; thus $P_{\alpha\beta}$ is the force per unit area in the β-direction acting on an element of surface pointing in the α-direction.

2.2. The principal independent variables; corresponding states analysis

For confined nano-phases, the number of system variables considerably exceeds those of temperature, pressure, and compo-sition for bulk phases. These additional variables include the com-position and structure of the adsorbent material, the size and shape of the pores, their morphology and topology, wall rough-ness, *etc.* In view of this added complexity, it is instructive to con-sider first a simple system in which the pores are of simple geometry with smooth walls, while the adsorbate molecules can be treated as effectively spherical as far as their intermolecular interactions are concerned. We consider an adsorbate (a) that is a pure substance confined in a slit-shaped pore of width H. There are two kinds of intermolecular potential energies involved, adsorbate–adsorbate, $u_{aa}(r)$, and adsorbate-solid (s), $u_{as}(r)$. For the interaction of a single adsorbate molecule with the solid sur-face, the structureless 10-4-3 potential of Steele [5,6] is often a good approximation,

$$
u_{as}(z) = 2\pi\rho_s \sigma_{as}^2 \varepsilon_{as} \Delta \left[\frac{2}{5} \left(\frac{\sigma_{as}}{z} \right)^{10} - \left(\frac{\sigma_{as}}{z} \right)^4 - \left(\frac{\sigma_{as}^4}{3\Delta(z + 0.61\Delta)^3} \right)^3 \right].
\tag{3}
$$

This expression is arrived at by integrating the pair interactions between an adsorbate molecule located at distance z from the pore wall over the positions of the atoms in the solid with which it interacts, and assuming that the solid atoms are arranged in layers separated by distance Δ, as in graphite. In this expression, ρ_s is the number of solid atoms per unit volume, and σ_{as} and ε_{as} are the usual parameters of size and energy well depth in the intermolec-ular pair potential energy, here taken to be the Lennard–Jones (12,6) model. Thus the 10-4-3 model treats the wall as structure-less. This model ignores corrugations in the surface and is generally