

## Adsorption Isotherms with Hysteresis Loops

The understanding of adsorption isotherms is important in the solution of a large class of industrial problems. Many of these problems are of current research interest. One particular example is the safe and efficient storage, handling, and transportation of gasses. It has been proposed that flammable gasses could be adsorbed onto a variety of substances prior to transportation, and then released into cylinders after their arrival<sup>1</sup>. The success of such a method hinges upon being able to store large quantities of gasses in the pores of the sorbent material. In this process, the phenomenon of capillary condensation becomes important. The gas first adsorbs in the pores at a low density. After a sufficient amount of gas has been supplied, it spontaneously condenses into a liquid-like state inside the pores. In some cases, the adsorbed liquid may be more dense than the corresponding bulk liquid, allowing large amounts to be stored inside the material. In order to make an informed choice of material for the storage and transport of gasses by this method, one first must have knowledge of its adsorption behavior. This is just one of many examples of problems which require a knowledge of adsorption phenomena.

Most analysis of adsorption equilibria begins with the classification of the isotherms. In 1985, the IUPAC developed a standard classification that consisted of six general isotherm types<sup>2,3</sup>. These isotherms included five classical isotherm shapes, plus a sixth that involved steps. In the case of adsorption where capillary condensation occurs, hysteresis loops appear. Very recently, these hysteresis loops have been classified in a way similar to the IUPAC adsorption isotherm scheme<sup>4</sup> (Figure 1). Classical explanations of hysteresis are based on a change of geometry during the adsorption and desorption process, and the Kelvin equation<sup>5</sup> has been used for theoretical justification. However, the Kelvin equation is a macroscopic argument. The goal of this work is to reproduce the hysteresis isotherm classification with molecular calculations. The primary tool in this study is lattice density functional theory (DFT), a mathematically simple technique that is based on the Ono-Kondo equations<sup>6</sup>.

In this work, a single slitlike pore with variable length and width is modelled. The pore is allowed to adsorb molecules with nearest neighbor interactions, and the molecule-molecule and molecule-wall potentials are explicitly taken into account.

The results of the work show that the DFT model is capable of duplicating the four classes of hysteresis isotherms that have been suggested in the literature. In addition, a fifth class

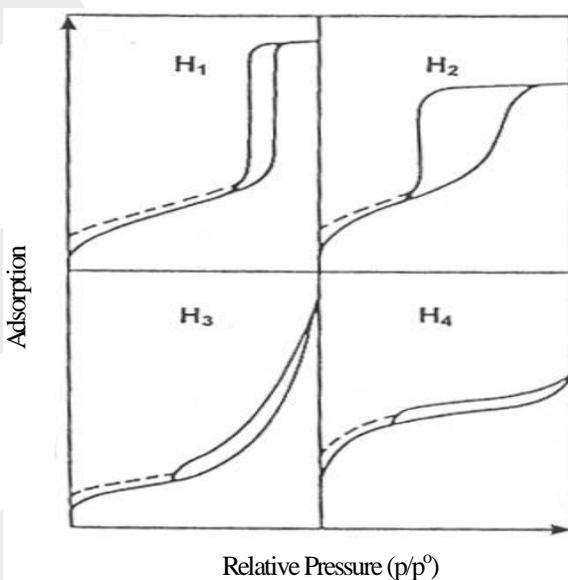
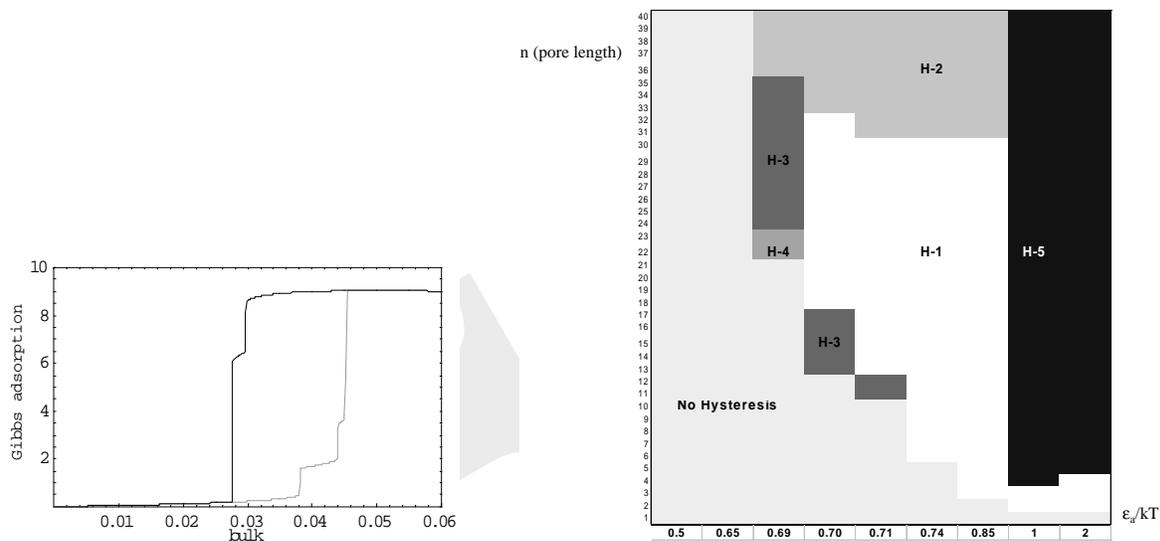


Figure 1: The four classifications of adsorption isotherms with hysteresis loops.



(a) An adsorption isotherm with steps.

(b) The dependence of adsorption hysteresis on pore length and interaction energy.

Figure 2: DFT predictions of hysteresis loops.

of isotherms was predicted, as shown in Figure 2(a). These new isotherms have steps on the adsorption and/or desorption branch of the hysteresis loop. There is some evidence of their existence in experimental systems in the literature<sup>7</sup>.

Furthermore, the dependence of the hysteresis loop class on both pore length and molecule-wall interaction energy was studied; these results are shown in Figure 2(b). It was shown that as the energy and/or length was increased, hysteresis would first appear and then change from one class to another. These results will be important in the design of industrial processes involving adsorption phenomena.

<sup>1</sup>Biloe, S.; Goetz, V.; Mauran, S. *Carbon* **2001**, 39, 1653.

<sup>2</sup>IUPAC Recommendations *Pure Appl. Chem.* **1985**, 57, 603.

<sup>3</sup>IUPAC Recommendations *Pure Appl. Chem.* **1994**, 66, 1739.

<sup>4</sup>Rouquerol, F.; Rouquerol, J.; Sing, K *Adsorption by Powders & Porous Solids*; Academic Press: San Diego, 1999.

<sup>5</sup>Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*, 3rd ed.; Marcel Dekker: New York, 1997; Chapter 6.

<sup>6</sup>Ono, S.; Kondo, S. *Molecular Theory of Surface Tension in Liquids*; Springer: Gottingen, 1960.

<sup>7</sup>Bordere, S.; Llewellyn, P. L.; Rouquerol, F.; Rouquerol, J. *Langmuir* **1998**, 4217.