

# MOLECULAR MODELING OF EQUILIBRIUM OF SIMPLE FLUIDS IN CARBONS: THE SLIT PORE MODEL REVISITED

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## Introduction

The modeling of fluid equilibrium in confined spaces and, in particular, the micropores of carbon, is a problem of long standing importance. Most of the early models, such as those based on the Langmuir, BET, Kelvin and Dubinin theories [1-3], neglect the texture of the force field arising from the fluid solid interaction, and are therefore semi-empirical or not predictive. In the last two decades, however, molecular simulation has emerged [4,5] as a powerful tool for the investigation of adsorption in confined spaces, permitting first principles based predictions that can be used to interpret experimental data. From a theoretical standpoint the most successful approach is that of density functional theory [6], that is now popular from a viewpoint of characterization [7-9] as well as prediction of adsorption behavior [10,11] in systems involving simple Lennard Jones fluids. All of these methods rely on a structural model that imbeds heterogeneity, and can be used to predict fluid equilibrium following the generalized adsorption isotherm, or GAI [7-9,11].

## Structural Modeling of Carbons

For carbons the slit pore model is the most common, and has a long history [12] stemming from early x-ray diffraction based concepts of disorganized turbostratic crystallites as basic structural units (or BSU's), with the pore walls comprising the BSU's or parts thereof. However, as currently used the slit pore model assumes infinitely thick pore walls, and thereby neglects short-range disorder. More recent models develop molecular level alternatives, such as those based on reverse Monte Carlo Simulation [13-15] fits of x-ray diffraction determined structure factors, which do incorporate short-range disorder. A key difference between the different approaches is the level of such disorder achieved, and use of additional techniques to probe the short-range structure may be needed to refine the methods and distinguish between them. More significantly, they are also computationally intensive, and therefore not yet amenable for routine use.

In our own laboratory we have shown that the slit pore model can be resurrected by discarding the commonly used infinitely thick wall assumption, and incorporating short

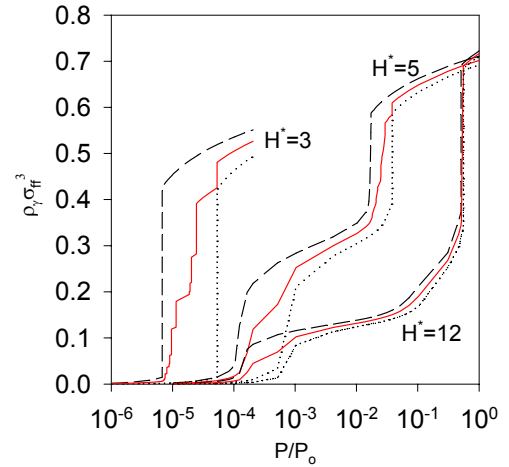
range disorder via a pore wall thickness distribution. The motivation for this derives from a new relation [11]

$$\gamma = \frac{2N_o}{\rho_s M_c S_g} = \frac{2629.9}{S_g} = \frac{0.1315}{\int_0^\infty [f_\mu(H)/H] dH} \quad (1)$$

between the mean number of graphene layers per pore wall,  $\gamma$ , and the surface area,  $S_g$  ( $\text{m}^2/\text{g}$ ) or the pore volume distribution,  $f_\mu(H)$ . Here  $N_o$  is the Avogadro number,  $\rho_s$  is the surface density of carbon atoms in a layer and  $M_c$  is atomic weight of carbon. Since most carbons have surface areas in the range 1200-2000  $\text{m}^2/\text{g}$ , it is evident that the pore walls can have only about 1-2 layers on average, suggesting that the infinitely thick wall assumption might be problematic. Indeed DFT calculations [11] show that it leads to overprediction of adsorbed amount by as much as a factor of 2 at low pressures. For such small thicknesses, fluctuations in the number of wall layers are also of concern, and eq. (1) is replaced by a modified generalized adsorption isotherm (GAI)

$$\hat{\rho}(\rho) = \sum_{\ell=1}^{\infty} p(\ell) \sum_{m=1}^{\infty} p(m) \int_0^\infty \rho_{\ell m}(H, P) f_\mu(H) dH \quad (2)$$

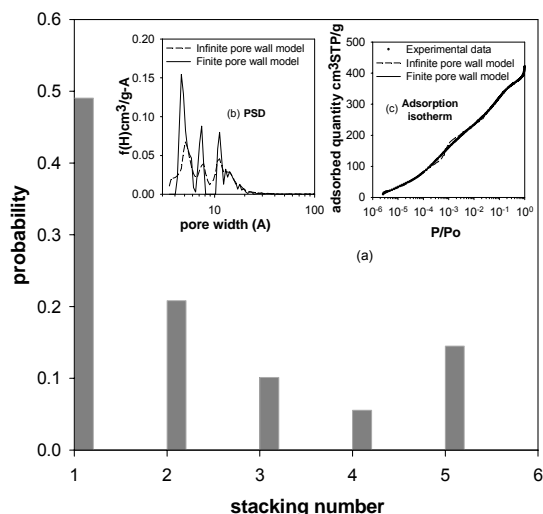
where  $\rho_{\ell m}(H, P)$  is the local DFT isotherm in a pore of width  $H$ , with left wall having  $\ell$  graphene planes and right wall having  $m$  graphene planes, and  $p(n)$  is the probability that a given pore wall has  $n$  graphene layers. In solving for the local isotherm using nonlocal density functional theory (NLDFT) the commonly used Steele 10-4-3 fluid-solid interaction potential is replaced by its finite wall counterpart [16]. The resulting isotherms incorporate the additional heterogeneity of the pore wall thickness, which mitigates the abrupt nature of the phase transitions at any pore size for sub-critical fluids. As an example Figure 1 depicts the isotherms for nitrogen at various pore widths [11], illustrating the more gradual nature of the phase transitions at a given pore size, due to the different transition pressures in pores having walls with different numbers of graphene layers. A Poisson distribution of the number of layers in a pore wall is assumed. In the computations an independent pore approach is used, which assumes that interaction between fluid molecules in neighboring pores is not of significance. NLDFT calculations [11] have confirmed that such interactions can indeed be neglected for small molecules such as argon and nitrogen, so that eq. (2) can be reliably used for characterization. This has been exploited in our laboratory as discussed below.



**Figure 1.** Comparison between predicted nitrogen isotherms for carbons having pore wall disorder with  $\gamma = 2$  (solid lines), and those for carbons having infinitely thick walls (dashed lines). Dotted lines represent the isotherms for pores with both walls having only one layer.

## Characterization of Carbons using the Modified Slit Pore Model

An attractive feature of our treatment is that the pore wall thickness distribution,  $\rho(n)$ , is correlated with the PSD,  $f_{\mu}(H)$  through eq. (1). This now permits solution of the otherwise difficult characterization problem of simultaneously determining the distributions  $\rho(n)$  and  $f_{\mu}(H)$  from adsorption data. Indeed, earlier characterization attempts considering finite pore walls have been largely *ad hoc*, utilizing arbitrary assumptions about the thickness of the confining walls [17], and have not resulted in a



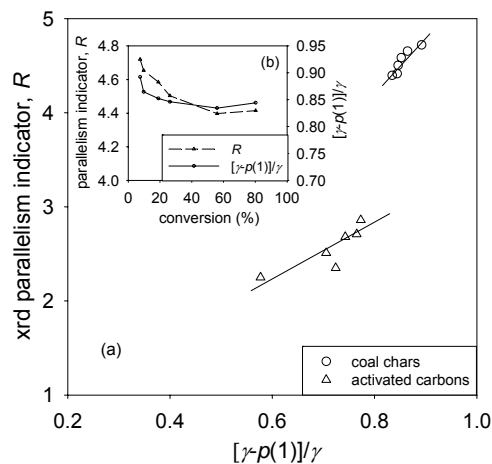
**Figure 2.** Pore wall thickness distribution of BPL activated carbon determined by argon adsorption.

viable solution. In our laboratory, however, considerable success has been achieved [18,19] in solving for  $\rho(n)$  and  $f_{\mu}(H)$  from adsorption data, by combining regularization with a genetic algorithm, with the local isotherm determined by the established Tarazona [6] DFT. As an example, Figure 2 depicts results obtained for BPL carbon, obtained using argon adsorption at 87 K, showing predominance of single layer walls. The pore size distribution in the left insert shows much sharper peaks in the finite wall case, with a shift towards narrow pores. Also the peak separations are close to the layer spacing (3.35 Å), suggesting that micropores may be defects or clusters of missing planes in crystallites. Further, as seen in the right inset, the S-shaped deviation in the isotherm

fit of the infinite wall thickness model in the  $P/P_0$  range  $10^{-4}$ - $10^{-3}$  is removed.

XRD studies on commercial activated carbons and coal chars prepared in our laboratory have yielded good correlation of the parallelism indicator with features of the pore wall thickness distribution. This parallelism indicator, as obtained from the 002 peak, is related to the fraction of planes that have at least one neighbour. In terms of our model this fraction is obtained as  $[\gamma - \rho(1)]/\gamma$ . As an example Figure 3 depicts the correlation obtained for some carbons and chars, providing support for the validity of the pore wall thickness distribution determined from argon adsorption.

The above results considerably extend the realism and value of the slit pore model. In on-going work we are using the approach to study the restructuring and pore wall thickening of BPL



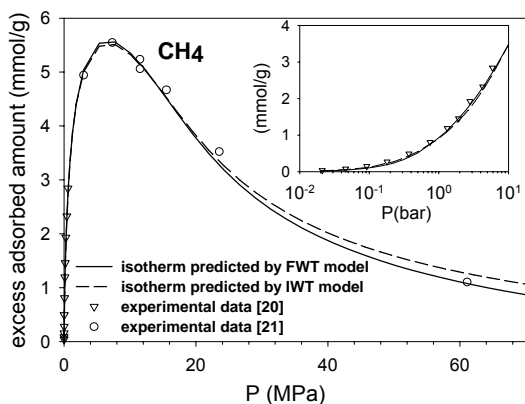
**Figure 3.** Correlation between XRD based parallelism indicator,  $R$ , and its counterpart  $[\gamma - \rho(1)]/\gamma$  determined by adsorption. Inset depicts their variation with conversion for partly oxidized char.

carbon with heat treatment. In addition, we are investigating a series of activated carbon fibres, to determine their structural characteristics using argon adsorption. The results will be reported.

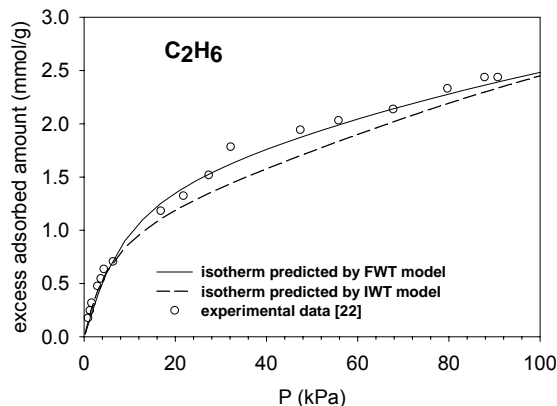
As discussed earlier, the above characterization is based on an independent pore model, as the effect of inter-pore interaction for fluid molecules in adjacent pores separated by thin walls has been shown to be insignificant for small molecules used in characterization [11]. In more recent work [19] the effect of this has been further investigated, by considering a model carbon with a uniform micropore width and bimodal pore wall thickness distribution, and constructing the argon isotherm while considering the inter-pore interaction. On inversion of this isotherm, while assuming the independent pore model, the correct pore size and pore wall thickness distribution could be recovered.

### Prediction of Adsorption Equilibrium

The prediction of the adsorption of supercritical gases in porous carbons, using characteristic parameters of their internal structure probed by gas adsorption, is an important issue. A key difficulty involved here has been the inadequacy of the models utilized for carbon structure. For simple fluids modelled as comprising of Lennard Jones particles, NLDFT may be readily used for isotherms prediction using the new finite wall thickness (FWT) approach. Figures 4 and 5 depict the predictions for adsorption of methane and ethane respectively in BPL carbon, illustrating the improved performance of the FWT approach compared to the infinite wall thickness (IWT) approach. The overprediction or underprediction by the IWT approach is related to two competing



**Figure 4.** Predicted and experimental adsorption isotherm of methane in BPL at 298 K. The right inset presents the isotherms up to 0.6 MPa. Solid line depicts predicted isotherm obtained from FWT model and dashed line represents that using IWT model. Open down triangle represent experimental data up to 0.6 MPa [20], and open circles that up to 60 MPa [21].



**Figure 5.** Predicted and experimental adsorption isotherms of ethane in BPL at 323 K. Solid line depicts predicted isotherm obtained from finitely wall thick model and dash line represents that using finitely thick wall model. Open open circles are experimental data up to 1 bar [22].

effects. On the one hand the higher density arising from the stronger potential field of the IWT model leads to a smaller pore volume determined from argon adsorption by this approach. On the other hand in isotherm prediction for another fluid the IWT again predicts a slightly higher density, although in the smaller pore volume determined by argon adsorption. These two effects combine to yield overprediction in some cases and underprediction in others. Figures 4 and 5 clearly show that the FWT approach offers a better alternative for carbon structure than the IWT model that lumps all heterogeneities into a single one comprising the pore size distribution.

## Conclusions

The above results demonstrate that adsorption can be reliably used to probe the physical structure of the solid phase in carbons, conventionally studied by x-ray diffraction. The good correspondence with xrd, combined with the sharp PSD peaks, suggests that the narrow micropores are defects within the same crystallite, most likely arising from missing portions of neighboring graphene sheets. Nevertheless, some influence of intercrystalline pore space, particularly in the larger pores beyond about 1 nm may be expected. Further, pore-pore correlation has been shown to have a negligible effect on results of pore size and pore wall thickness distributions obtained from interpretation of argon adsorption at 87 K using our current approach. Finally, it has been illustrated that our current approach offers considerable improvement over the infinitely thick wall model, and enables one to use the approach predictively for a given carbon, after determining structural parameters by argon adsorption.

## References

- [1] Gregg, S.J., Sing, K.S.W., *Adsorption, Surface Area and Porosity*, Academic Press: London (1982).
- [2] Yang, R.T., *Gas Separation by Adsorption Processes*, Butterworths: Boston (1987).
- [3] Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, John Wiley: New York (1984).
- [4] Nicholson, D., and Parsonage, N., *Computer Simulation and the Statistical Mechanics of Adsorption*, Academic Press: New York (1982).
- [5] Allen, M.P., and Tildesley, D.J., *Computer Simulation of Liquids*, Oxford University Press: New York (1987).
- [6] Tarazona, P., *Phys. Rev. A*, **31**, 2672 (1985); **32**, 3148 (1985). Tarazona P., Marconi, U.M.B., and Evans, R., *Mol. Phys.*, **60**, 573 (1987).
- [7] Seaton, N. A., Walton, J.P.R.B., and Quirke, N., *Carbon*, **27**, 853 (1989).
- [8] Lastoskie C.; Gubbins K.E., and Quirke, N., *Langmuir*, **9**, 2693 (1993).
- [9] Vishnyakov, A., Ravikovitch, P.I. and Neimark, A.V., *Langmuir*, **15**, 8736 (1999).
- [10] Bhatia, S.K., *Langmuir*, **14**, 6231 (1998).
- [11] Bhatia, S.K., *Langmuir*, **18**, 6845 (2002).
- [12] Bandosz, T.J., Biggs, M.J., Gubbins, K.E., Hattori, Y., Liyama, T., Kaneko, K., Pkunic, J., and Thomson, K.T., *Chem. Phys. Carbon*, **28**, 41 (2003).
- [13] O'Malley, B., Snook, I. and McCulloch, D., *Phys. Rev. B*, **57**, 14148 (1998).

- [14] Thomson, K.T., and K.E. Gubbins, *Langmuir*, **16**, 5761 (2000).
- [15] Pikunic, J., Clinard, C., Cohaout, N., Gubbins, K.E., Guet, J.-M., Pellenq, R.J.-M., Rannou, I., and Rouzaud, J.-N., *Langmuir*, **19**, 8565 (2003).
- [16] Steele, W. A., *Surf. Sci.*, **36**, 317 (1973).
- [17] Ravikovitch, P. I.; Jagiello J.; Tolles, D. ; Neimark A. V. Carbon'01, International Conference on Carbon, Lexington, (**2001**).
- [18] Nguyen, T.X., and Bhatia, S.K., *Langmuir*, submitted (2003).
- [19] Nguyen, T.X., and Bhatia, S.K., *J. Phys. Chem. B*, submitted (2004).
- [20] LeVan, M. D., and Pigorini, G., in *Foundations of Molecular Modeling and Simulation*, Proceedings of the First International Conference on Molecular modeling and Simulation, Keystone, Colorado, July 23-28 (2000).
- [21] Vidal, D., Malbrunot, L., Guengant, L., and Vermesse, *J. Rev. Sci. Instrum.*, **61**, 1314.
- [22] Russel, B. P., and LeVan, M. D., *Ind. Eng. Chem. Res.*, **36**, 2380 (1997).