A MODIFIED HORVATH-KAWAZOE METHOD FOR MICROPOROUS SIZE ANALYSIS

Christian M. Lastoskie
Department of Chemical Engineering
Michigan State University
East Lansing, MI 48824-1226 USA

ABSTRACT

The Horvath-Kawazoe (HK) method is a semi-empirical, analytic model of adsorption in micropores that is commonly used for determining the pore size distributions (PSDs) of microporous materials. The HK method is a substantial improvement over classical adsorption models (e.g. Kelvin-based methods) in that the adsorbate potential interactions with the adsorbent surfaces are explicitly accounted for. One of the principal shortcomings of the original HK method, however, is that the mean potential energy change due to adsorption is calculated from an unweighted average over position within the micropore. It is known from molecular simulation studies of adsorption at subcritical temperatures that the local density of the adsorbate in the pore varies strongly with position due to fluid layering near the pore walls. The omission of this structure dependence from the original HK model leads to an overestimation of micropore filling pressures relative to the exact filling pressures calculated from molecular simulations.

In this paper, a modified HK method is presented which accounts for spatial variations in the density profile of a fluid (argon) adsorbed within a carbon slit pore. We compare the pore width/filling pressure correlations predicted by the original HK method, the modified HK method, and methods based upon statistical thermodynamics (density functional theory and Monte Carlo molecular simulation). The inclusion of the density profile weighting in the HK adsorption energy calculation improves the agreement between the HK model and the predictions of the statistical thermodynamics methods. Although the modified Horvath-Kawazoe adsorption model lacks the quantitative accuracy of the statistical thermodynamics approaches, it is numerically convenient for ease of application, and it has a sounder molecular basis than analytic adsorption models derived from the Kelvin equation.

1. INTRODUCTION

Gas sorption porosimetry is a standard method for the characterization of the pore size distribution (PSD) of porous solids. To interpret the experimental isotherm and obtain the adsorbent PSD, one must adopt a model for the pore structure, and a theory that estimates the adsorption that will occur in pores of a particular size. If the porous solid is represented as an array of independent, noninterconnected pores of uniform geometry and identical surface chemistry, then the excess adsorption, \( \Gamma(P) \), at bulk gas pressure \( P \) is given by the adsorption integral equation.
\[ \Gamma(P) = \int_{H_{\text{min}}}^{H_{\text{max}}} \Gamma(P,H) f(H) dH \] (1)

where \( \Gamma(P,H) \) is the excess adsorption for an adsorbent in which all the pores are of width \( H \); and \( f(H) \) is the pore size distribution of the material. The integration endpoints \( H_{\text{min}} \) and \( H_{\text{max}} \) correspond to the minimum and maximum pore widths present in the adsorbent. The adsorption integral of equation (1) is written in terms of a distribution of slit pore widths, a geometry frequently used to approximate the pore structure of activated carbons. For porous glasses, oxides, silicas, and other mineral adsorbents, the adsorption integral may be recast in terms of a distribution of pore radii \( f(R) \) for a model porous solid composed of noninterconnected cylindrical pores.

Within the constraints imposed by the assumed geometric model for the pore shape, the accuracy of the PSD obtained by the solution of equation (1) depends on the realism of the adsorption model \( \Gamma(P,H) \) that is adopted to describe the local isotherm. A variety of pore filling models have been proposed for representing the local isotherm. The classical approach has been to assume that the Kelvin equation, or a modified form of it, correctly predicts capillary condensation as a function of pore width [1]. It is known from experiments [2], and from comparisons with exact molecular simulation results for a variety of pore geometries [3-7], that the Kelvin and modified Kelvin (MK) equations predict pore filling pressures that are too large (see Figure 1). Consequently, Kelvin-based adsorption theories, when inserted into equation (1), give pore sizes that are too small. The error is significant for pore sizes below about 7.5 nm [2,5], and it becomes very large for micropores (i.e. pores smaller than 2.0 nm). In microporous adsorbents, dispersion interactions between the adsorbate and the atoms of the porous solid are greatly enhanced. Because the Kelvin-based adsorption models do not account for these enhanced gas-solid interactions, PSD analysis methods based upon the Kelvin equation are unreliable for the characterization of microporous solids.

An alternative to the classical thermodynamic model of pore filling is to use methods from statistical thermodynamics, such as density functional theory (DFT) [6,8] or Gibbs ensemble Monte Carlo molecular simulation (GEMC) [7,9] to calculate local isotherms for simple pore geometries (e.g. for slits or cylinders). These methods explicitly incorporate the gas-solid potential interaction into the adsorption calculation, and hence they yield more realistic local isotherms for modeling adsorption in micropores. Several independent studies have demonstrated that DFT is superior to the Kelvin equation for micropore PSD analysis [6,10-11]. Because detailed morphologies of porous adsorbents like activated carbons are usually not known, molecular simulation results for ideal model adsorbents are frequently used as the standard for evaluating other pore filling models. One such comparison is shown in Figure 1 for nitrogen adsorption on model carbon slit pores at 77 K. The modified Kelvin method (MK) severely overestimates the micropore filling pressures, whereas the \( \Phi \) function agrees well with the "exact" results computed by molecular simulation.

The principal drawback to the classical adsorption methods is the lack of correlation with Monte Carlo molecular simulation, whereas accounting for dispersion through the approach proposed by Horvath and Kassak [12] for adsorption on carbon beds can yield a useful correlation. This means that the MK equation is an unreliable tool for the characterization of microporous solids.

\[
\ln \left( \frac{P}{P_0} \right) = \frac{\Phi(H)}{RT}
\]

In equation (2), \( P \) is the bulk gas pressure; \( P_0 \) is the saturation vapor pressure; \( \gamma \) is the capillary condensation pressure at the solid-liquid interface; \( \beta \) is a correction factor; and \( T \) is the temperature. The correlative parameter \( \Phi(H) \) is computed from the accessible volume of the pore:

\[
\Phi(H) = \frac{\int_{H}^{H_{-\sigma_\Phi}} \phi(z) dz}{\int_{H_{-\sigma_\Phi}}^{H-\sigma_\Phi} \phi(z) dz}
\]
all the pores are of width $H$; and

Figure 1: Relation between filling pressure and pore width predicted by the modified Kelvin equation (MK), the Horvath-Kawazoe method (HK), density functional theory (DFT), and molecular simulation (points) for nitrogen adsorption in carbon slits at 77 K [11].

filling pressures, whereas the DFT method yields a pore filling correlation in close agreement with the “exact” results computed from GEMC molecular simulation [7].

The principal drawback of the DFT method is that it is computationally intensive relative to the classical adsorption models, although it is still much less compute-intensive than full Monte Carlo molecular simulation. A semianalytic adsorption model that retains computational efficiency while accounting for gas-solid potential interactions in micropores was originally proposed by Horvath and Kawazoe [12]. In the Horvath-Kawazoe or HK method, a pore filling correlation is obtained by calculating the mean heat of adsorption $\bar{\Phi}$ required to transfer an adsorbate molecule from the gas phase to the condensed phase in a slit pore of width $H$:

$$\ln\left(\frac{P_c}{P_0}\right) = \frac{\bar{\Phi}(H)}{RT}$$  \hspace{1cm} (2)

In equation (2), $P_0$ is the bulk gas saturation pressure; $P_c$ is the pore filling pressure; $R$ is the gas constant; and $T$ is the temperature. In the original HK method, the mean heat of adsorption is computed from an unweighted average of the gas-solid interaction potential taken over the accessible volume of the pore:

$$\bar{\Phi} = \frac{\int_{\sigma_f}^{H - \sigma_f} \phi(z)dz}{\int_{\sigma_f}^{H - \sigma_f} dz} = \frac{\int_{0}^{H - \sigma_f} \phi(z)dz}{H - 2\sigma_f}$$  \hspace{1cm} (3)
In equation (3), $\phi$ is the gas-solid potential for an adsorbate molecule located at position $z$ in a slit pore of physical width $H$; i.e., a pore in which the nuclei of the surface layer solid atoms are located at $z=0$ and $z=H$. The effective gas-solid molecular diameter, $\sigma_{eff}$, is calculated from the arithmetic mean of the diameter of the adsorbate molecule and the adsorbent surface atom. The pore filling correlation predicted by the original HK equation for nitrogen adsorption in carbon slit pores at 77 K is shown in Figure 1. It is seen that the HK method gives improved micropore filling predictions compared to Kelvin-based methods. However, the HK model still substantially overestimates the micropore filling pressures given by molecular simulation. The original HK methodology of equations (2) and (3) was subsequently modified for cylindrical [13] and spherical [14] pore geometries, with essentially the same result: the HK model is superior to the Kelvin equation for micropore characterization, but inferior to DFT or simulation methods [10,11].

The failure of the HK method, as originally formulated, to accurately predict micropore filling pressures can be understood by considering the gas-solid potential $\phi(z)$ in a carbon slit pore, and the local adsorbed fluid density profile $\rho(z)$ that arises in the pore on account of this potential. In Figure 2, the gas-solid potential $\phi^* = \phi/\varepsilon_{eff}$ for three different slit pore widths $H^* = H/\sigma_{eff}$ is shown in Figure 2 for nitrogen adsorption in a carbon slit pore at 77 K; $\varepsilon_{eff}$ and $\sigma_{eff}$ are the Lennard-Jones well depth and molecular diameter for nitrogen pairs. The gas-solid potential is shown as a function of the center-of-mass position $z^* = z/\sigma_{eff}$ of the nitrogen molecule, where $z=0$ is the centerline of the slit pore. For each case, the gas-solid potential is calculated using the 10-4-3 potential [15] to represent the interaction between the nitrogen molecule and the graphite slabs that bound the slit pore. It can be seen from Figure 2 that a large potential well is present in the pore at a distance of one molecular diameter from either pore wall. It is at this location that the contact layer (monolayer) of adsorbate will form within the slit. The region of the slit pore near the centerline may also have a negative (i.e. attractive) gas-solid potential, depending upon the width of the pore. For supermicropores (e.g. $H^*=4$), the gas-solid potential is attractive throughout the entire accessible pore volume; for ultramicropores (e.g. $H^*=2$), the two potential minima coalesce into a single, deeper potential well.

Because of the presence of strong potential wells for adsorption at low temperatures, the adsorbed fluid adopts a highly structured local density profile, as shown in Figure 3 for argon adsorption in a carbon slit pore of width $H^*=6$. The local density profile $\rho^* = \rho/\rho_{eff}$ is computed from DFT and exhibits strong monolayer peaks near $z^*=1$ and $z^*=5$. Secondary peaks in $\rho(z)$ form at positions $z^*=2, 3$ and 4 due to structuring of the condensate adjacent to the monolayer. Similar condensed-phase density profiles are observed in slit pores of other widths. The structure of the local density profile given by DFT has been validated against molecular simulation calculations and has been found to be quantitatively accurate over a wide range of pore sizes and bulk gas pressures.

In the original HK method [12], the mean heat of adsorption $\bar{\phi}$ is calculated from an unweighted average of the gas-solid interaction potential measured over the accessible volume of the pore. This prescription implicitly assumes that the adsorbate density is uniform everywhere in the accessible region in Figure 3. However, in adsorbed fluid density profile and troughs resulting from the high degree of ordering in the density in the monolayer region, the heat of adsorption computed...
molecule located at position $z$ in a slit the surface layer solid atoms are meter, $\sigma_f$, is calculated from the adsorbent surface atom. The for nitrogen adsorption in carbon method gives improved micropore However, the HK model still by molecular simulation. The nitogen pair for cylindrical [13] result: the HK model is superior to or to DFT or simulation methods.

Figure 2: Gas-solid potentials for nitrogen adsorption at 77 K in carbon slit pores of different width.

...to accurately predict micropore solid potential $\phi(z)$ in a carbon slit... in the pore on account of this three different slit pore widths $H^*$ in slit pore at 77 K; $\sigma_f$ and $\sigma_{ff}$ are... potential of the nitrogen molecule, where... potential is calculated using the nitrogen molecule and the graphite... a large potential well is present in pore wall. It is at this location that... slit. The region of the slit pore gas-solid potential, depending upon... potential is attractive (e.g., $H^*=2$), the two potential... adsorption at low temperatures, the... shown in Figure 3 for argon... density profile $\rho^*=\rho_0 \sigma_f^2$ is computed... $z^*=5$. Secondary peaks in $\rho(z)$ ensate adjacent to the monolayer,... slit pores of other widths. The been validated against molecularly accurate over a wide range of... adsorption $\bar{\phi}$ is calculated from an... range over the accessible volume of... the adsorbate density is uniform everywhere in the accessible region of the slit pore, as shown schematically by the solid line in Figure 3. However, it can be clearly seen from the DFT results of Figure 3 that the adsorbed fluid density profile is not uniform, but is in fact highly structured and contains peaks and troughs resulting from the monolayer adsorption well and fluid layering. By neglecting the high degree of ordering in the adsorbed fluid, and in particular by undercounting the adsorbate density in the monolayer region, the HK method, as originally posed, underestimates the mean heat of adsorption computed by equation (3), and thus overestimates the micropore filling...
pressures calculated from equation (2). This leads to PSD analysis results obtained for the HK model in equation (1) that are less accurate than those given by DFT or molecular simulation.

2. THE MODIFIED HORVATH-KAWAZOE METHOD

The neglect of adsorbed fluid structuring principally accounts for the shortcomings of the original HK method, and also suggests a corrective measure. If the density profile, or a reasonable representation of it, were to be included in the calculation of the mean heat of adsorption $\bar{\phi}$, then the HK pore filling correlation would more closely agree with the molecular simulation/DFT results. Thus, in our modified HK method we seek to evaluate the mean heat of adsorption from the density-weighted integral

$$\bar{\phi} = \frac{\int_{-\sigma_f}^{H_f - \sigma_f} \rho(z) \phi(z) dz}{\int_{-\sigma_f}^{H_f - \sigma_f} \rho(z) dz}$$

and use this result for $\bar{\phi}$ in equation (2). One difficulty in doing this is that a full statistical thermodynamics treatment is needed to obtain the adsorbate density profile in the slit pore. To retain the computational efficiency of the HK approach, we seek a mathematical function that realistically represents $\rho(z)$ in accordance with the DFT results, so that we can evaluate equation (4) for other probe gas/adsorbent systems without having to repeat the DFT calculations. The sharply peaked, highly structured density profile that is observed in Figure 3 is characteristic of adsorption at low temperature, and suggests that a sum of Gaussian distributions might satisfactorily represent the adsorbate density profile. The number of Gaussian distributions required for a pore of a given size is equal to the number of peaks that appear in the condensed fluid density profile of the pore.

For pore widths that have density profiles with more than two peaks (e.g. the $H^*=6$ pore in Figure 3), we have the option of fitting the height and variance of each Gaussian distribution separately. Also, we could in principle fit the Gaussian parameters for the density profile at each pore width independently of the other pore widths. However, this would lead to a large and unwieldy parameter set, and would make a corresponding states-type generalization of the modified HK method for other adsorbate/adsorbent systems very difficult. Therefore, the local density profile is modeled as an $n$-modal Gaussian distribution, where each mode $i$ of the distribution has the same height $\alpha$ and variance $\tau$, but a different mean position $\mu_i$ in the slit pore:

$$\rho(z) = \alpha \sum_{i=1}^{n} \exp \left[ \frac{-(z - \mu_i)^2}{2\tau^2} \right]$$

Although this choice of fitting the Gaussian fits to the DFT density profiles were calculated from 200 torr at 77 K, using a spacing of 0.5 torr. Details of the DFT calculation are described elsewhere. Gaussian peak height $\alpha$ was equal to 1, and peak height (e.g. the peak center) squares error criterion was then used to fit each density profile according to

$$n = \text{int}(H^* + 0.5) - 1$$

where int($x$) is the rounded integer to half of a molecular diameter, 3.5$\leq H^*$$<4.5$; and so on. The best Gaussian parameter values for the density fits are shown in Figure 4 for the first two multiples of the adsorbate dimension. Reasonably well using a simple Gaussian distribution to represent the multi-layer adsorbate that are too thick and too narrow to separate $(\alpha, \tau)$ values for this set of parameters. Alternatively, on
analysis results obtained for the HK DFT or molecular simulation.

Although this choice of fitting function somewhat diminishes the overall accuracy of the Gaussian fits to the DFT density profiles, it simplifies the model to a manageable number of parameters. An additional simplification is achieved by spacing the mean positions of the Gaussian distributions exactly one adsorbate molecular diameter \(\sigma_f\) apart; i.e.

\[
\mu_i = \sigma_{sf} + (i - 1)\sigma_f
\]

for each additional Gaussian distribution inward from the monolayer peak to the pore centerline. This placement strategy is consistent with the peak positions observed for DFT density profiles in pores of different size. To implement the modified HK method, we therefore need only find the pair of \((\alpha, \tau)\) values in equation (5) that give the best fit to the adsorbate density profiles over the range of micropore widths of interest for PSD analysis.

3. RESULTS AND DISCUSSION

Sorbed argon density profiles from DFT were fit for a set of 21 different graphitic carbon slit pore widths spanning the pore size range \(H^*\) from 2 to 6 (0.68 to 2.04 nm). All of the density profiles were calculated from DFT for supercooled liquid argon at its saturation pressure of 229 torr at 77 K, using a spacing interval of 0.01\(\sigma_f\) for the solution of \(\alpha(z)\) at each pore width. Details of the DFT calculations are reported elsewhere. The optimal value of the uniform Gaussian peak height \(\alpha\) was constrained so as to give the best agreement with the monolayer peak height (e.g. the peak centered at \(z^*\)=1 in Figure 3) in the set of density profiles. A sum-of-squares error criterion was then used to determine the best value of the variance \(\tau\) to represent the 15 density profiles according to equations (5) and (6). The number of Gaussian distributions \(n\) used to fit each density profile was determined from the formula

\[
n = \text{int}\left(\frac{H^*}{0.5}\right) - 1
\]

where \(\text{int}(x)\) is the rounded integer value of \(x\). Equation (7) assigns an additional Gaussian distribution to the fitting function whenever the dimensionless pore width is greater than or equal to half of a molecular diameter, so that \(n = 1\) for \(H^* < 2.5\); \(n = 2\) for \(2.5 \leq H^* < 5.5\); \(n = 3\) for \(3.5 \leq H^* < 4.5\); and so on. The best overall fit to the set of local density profiles was obtained for Gaussian parameter values of \(\alpha^* = \alpha_0 \sigma^3 = 7.48\) and \(\tau^* = \tau_0 \sigma = 0.0375\). The Gaussian distribution fits are shown in Figure 4 for four different pore sizes. For pore widths that are integral multiples of the adsorbate diameter (Figure 4a-b), the adsorbate density profiles can be fit reasonably well using a simple sum of uniform Gaussian distributions. Because of the aforementioned constraint imposed in matching the height of the monolayer peaks, the model tends to represent the multilayer peaks toward the center of the pore with Gaussian distributions that are too tall and too narrow. A better fit to the multilayer peaks could be obtained by using separate \((\alpha, \tau)\) values for this region of the pore, but this would introduce additional unwanted parameters. Alternatively, one could remove the constraint of matching the Gaussian peak
height with the monolayer peak height, but this would markedly worsen the fit of the Gaussian distribution in the monolayer region, where the bulk of the contribution to the mean heat of adsorption $\tilde{\varphi}$ occurs as calculated using equation (4). Thus, it was decided to enforce the constraint of matching the monolayer peak height, so as to achieve the best possible accounting of the adsorption energy of the densely packed argon molecules adsorbed in the monolayer.

For pore widths that are not integral multiples of adsorbate diameter (Figure 4c-d), the Gaussian fits are more inexact, due to the mismatch of using an integral number of Gaussian distributions to represent the local density profile in a pore of nonintegral dimensionless pore width. Nonetheless, the simple sum of uniform Gaussians portrays the adsorbate density profiles much as in the original HK method (as in Figure 5).

The filling pressure comparison and equation (4) for the modified HK method is shown in Figure 5. The pore filling pressures are enhanced by the potential [12] and the potential filling pressures are included in the literature. It is found that the sums of Gaussians, the accuracy of the integration.

As in the case of the original HK adsorption mechanism, where the pressure, and completely full (Figure 4a) or underfilled (Figure 4b) for the effects of precondensation. In this respect, the modified HK method is more applicable to a single most important aspect of the behavior of the pressure at which pore filling occurs as a function of filling pressures.

**Figure 4:** Local density profiles for argon adsorption in carbon slits at 77 K and 229 torr. (a) $H^*=3$; (b) $H^*=4$; (c) $H^*=3.25$; (d) $H^*=3.5$.

**Figure 5:** Comparison of filling pressure for argon adsorption at 77 K using the original HK and modified HK methods.
...worsen the fit of the Gaussian contribution to the mean heat of adsorption, it was decided to enforce the requirement of the best possible accounting for adsorption in the monolayer.

(b) for a number of Gaussian distributions not integral dimensionless pore radii.

As in the case of the original HK method, the modified HK model assumes a step-like adsorption mechanism, wherein a slit pore is completely empty at pressures below its filling pressure, and completely full (i.e., at a liquid-like density) at pressures above its filling pressure. In this respect, the modified HK method is inferior to the DFT adsorption model, which includes the effects of precondensation film growth in the local adsorption isotherm. However, the modified HK method is more computationally efficient than DFT, and it realistically models the single most important aspect of the adsorption isotherm for sorbent characterization, namely the pressure at which pore filling occurs. The modified HK method is clearly superior to the original HK and Kelvin-based pore filling models, which severely overestimate micropore filling pressures.

Figure 5: Comparison of filling pressure correlations for argon adsorption in carbon slit pores at 77 K using the original HK method, modified HK method, and DFT.
4. CONCLUSION

The Horvath-Kawazoe method, as originally posed, is unsuitable for the analysis of micropore PSDs because it greatly overestimates micropore filling pressures. By modifying the calculation of the mean heat of adsorption in the HK method to properly take into account the nonuniform adsorbate density profile in the micropore, the HK pore filling correlation can be brought into close agreement with the exact pore filling correlation given by DFT and molecular simulation. The modified HK method also retains the advantageous computational efficiency of the original HK method.

A modified HK method was presented in this paper for modeling argon adsorption in carbon slit pores at 77 K. A more general correlation, one that relates the fitted Gaussian parameters (α, τ) of the density profile to the temperature and characteristics of the gas-solid potential, is desirable so that the modified HK method may be extended to other probe gas systems of interest. This generalized correlation is currently under development and will be reported in an upcoming publication in the near future [16].

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LITERATURE CITED


Further evidences of microporous solids.

J. García-Martínez, D. Cazorla, Departamento de Química Inorgánica, Spain.

Porous texture characterisation using N2 adsorption at 77K and CO2 adsorption at 273K, data obtained from crystalline materials and porous carbons, can be found mainly in the framework of the zeolite family, where the micropores are significantly smaller. This is because measuring narrow micropores and nanopores is very difficult, as the total micropore volume and total area used to characterise porous solids is.

1. INTRODUCTION

Characterisation of porous materials is done in two main ways. The first way is to determine, or at least, infer the micropore volume and area of the porous material. In many cases, the micropores are the most widely used due to their importance for specific applications. One of the main advantages of using microporous materials is that they are sensitive to the whole range of the space where the adsorption is taking place, and this is why they are most used. One of its main advantages is that it is very sensitive to the whole range of partial pressures used to characterise the porous material.

To avoid the above problem, other adsorbents are used, such as 
4.2K[5,6] and CO2 adsorption at 273K for the whole range of partial pressures. This is the basic procedure for the characterisation of microporous materials.

Recently, both the fundamental studies of microporous materials have been used to study the adsorption properties. From studies conducted on the adsorption of nitrogen at 77K and at this temperature, the micropores can be studied on the adsorption properties. On the other hand, the adsorption properties of carbon materials at 77K can be studied on the adsorption properties of carbon materials.

A confirmation, as well as the number of studies conducted, is that the adsorption properties of carbon materials at 77K can be studied on the adsorption properties of carbon materials. In this sense, two main reasons can be identified:

1. The micropore structure [14-17]. On the other hand, the study focuses on the comp...