Ising model-modified kelvin analysis (IMMKA) for the prediction of water adsorption equilibrium and assessment of contact angle in carbon micropores

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Ising Model-Modified Kelvin Analysis (IMMKA) for the Prediction of Water Adsorption Equilibrium and Assessment of Contact Angle in Carbon Micropores

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ABSTRACT The unpredictable nature of the interaction of water molecules with carbon surfaces is evident in the wide-ranging behavior observed in simple macroscopic observations such as contact angle. Complex fluid-solid and fluid-fluid interactions can convolute the observed behavior and when coupled with confinement at the nanoscale, large deviations might be expected in predictions via macroscopic properties. However, by delivering a quantitative description of water adsorption in microporous carbon, this study demonstrates that macroscopic features can predict nanoscale behavior of confined water. Furthermore, through introduction of nanocapillarity and nanowetting, an Ising-Model-Modified-Kelvin Analysis (IMMKA) for water adsorption is proposed, interpreted and validated.

1.0 INTRODUCTION

The unique molecular properties of water generate intriguing features at the nanoscale that can translate into hydrophilic, hydrophobic and even superhydrophobic behavior [1]. At the macroscale where continuum analysis is applicable, fluid mechanics can be applied to assess experimental observations of water with surfaces. However, when significant surface interactions intrude, coupling fluid-solid with fluid-fluid behavior can be challenging. Additionally, the polar nature of water molecules yields interesting fluid-fluid behavior which can be paired with apolar or polar solid surfaces to produce a wide array of observable macroscopic features. These behaviors provide a challenge for fundamental understanding as well as opportunities for innovation with respect to friction and wear [2], hydration and electrochemical [3], as well as chemical application [4].

To further the fundamental understanding of water-carbon systems, a bridging of the continuum and molecular scales is required. To this end, a previous study [5] has utilized Ising model analysis (IMA) to successfully characterize water equilibrium features in carbon micropores that are defined by IUPAC to have width less than 2 nm. By assessing the two parameters of the Ising model applied to an isothermal system, relationships between these parameters and pore size have been established but not interpreted or validated. It is the purpose of this investigation to incorporate surface properties as well as heterogenous properties of real carbon networks with macroscopic properties such as capillarity at the nanometer level to deliver the interpretation and validation. Through application of a physical, structure-based model of microporous carbon, this study aims to:

- Interpret and rationalize previous findings obtained from data analysis.

- Validate the findings by comparison with other measured quantities in similar systems or with molecular simulation estimates of these quantities.

- Utilize macroscopic quantities such as surface tension and molecular level properties such as surface wetting and isosteric heat of adsorption to understand the nanoscale behavior of water confined in microporous carbon.

- Establish means for characterization and nanoscale prediction of water adsorption in carbon micropores.

- Establish a valid relationship for prediction of water adsorption equilibrium in carbon networks with narrow micropore size distributions.

To achieve these aims this study will firstly outline the structure of microporous carbon, then use results from data analysis to assess energies of interaction. The resulting assessment will be compared to molecular simulation and experimental measurement for validation. The interpretation will guide a structure-based model which will be proposed and validated by comparison with measurements from other studies.

2.0 THEORY

One of the primary aims of this study is to apply a structurally realistic model for microporous carbon in order to provide interpretation of water adsorption data. To this end, carbon structure will be briefly considered followed by its relationship with water adsorption features.

2.1 CARBON STRUCTURE

Thermal treatment of organic materials can produce amorphous carbon matrices containing graphitic microcrystallites mixed with amorphous carbon whose features are governed by this treatment [6,7]. Micropores are generally viewed as interstices between the graphitic units and therefore activating treatments can alter micropore size. Additionally, the network can contain hydrophilic functional groups of various amounts depending on precursor material and thermal history which can influence hydrophilicity [8,9] However, even in carbon networks that are mostly devoid of chemical functionality and referred to herein as non-functionalized carbon, the microporous network can offer affinity for water. Gubbins and coworkers [10,11 and other references cited in 8] have modeled non-functionalized carbon as ensembles of graphene layers which provide an idealization of the carbon network. In reality, heterogeneity and disorder in the form of pore size distribution, crystalline defects and possibly surface roughness could be introduced by activating treatments [12].

2.2 WATER ADSORPTION IN MICROPOROUS CARBON

The adsorption of water in non-functionalized, graphitic carbon is characterized by very little observed uptake at low loadings where Henry's law is observed [8,9]. This is traditionally interpreted as the carbon surface offering little affinity for water [13]. At moderate loadings and relative pressures, cooperative effects generated by significant adsorbate-adsorbate attraction promote further adsorption and the isotherm appears concave up and is marked by a point of inflection (POI). The relative pressure at which the POI occurs is sometimes used as an isotherm marker and is denoted as a_{POI} [5].

As filling of the pore continues, the isotherm tapers dramatically as the porous structure cannot accommodate further ingress and downwards concavity results. This yields a sigmoidal 'S'

shaped isotherm designated as Type V by IUPAC classification [13]. Ising model analysis (IMA) has been proposed to assess Type V isotherms [5]. This analysis allows for interaction between adsorbate (water) and the surface as a primary site for nucleation of subsequent processes. Additionally, it is indicative of solid-fluid interaction that is relevant at low pressure. Furthermore, it is equivalent to a Henry's law constant and it is represented as K_0 [5]. After primary site nucleation, secondary site interaction takes place and the nature of this interaction defines subsequent behavior [5]. Secondary site interaction is characterized by adsorbate-adsorbate (fluid-fluid) interactions, additional to fluid-solid. This interaction is represented by secondary site affinity parameter K_1 [5] which incorporates clustering and condensation-like phenomena.

Due to a lack of means for distinguishing clustering from condensation-like phenomena, a previous study [5] was undertaken to produce tools for this purpose. It has been demonstrated that the ratio K_1/K_0 which governs the isotherm steepness is a metric that is indicative of a system favoring condensation-like behavior over adsorption and clustering mechanisms [5]. Additionally, through the employment of Ising model analysis (IMA) to capture the form of the adsorption isotherm of a series of nominally non-functionalized activated carbon fiber (ACF) with narrow pore size distribution, governing relations for K_0 and K_1 were produced. This study will interpret these relations and reevaluate assessments made in the prior study [5].

3.0 RESULTS AND DISCUSSION

In a previous study [5], analysis via application of IMA to data for a series of ACF has yielded relationships for isotherm parameters and pore size that include components that are Kelvin-like

(inversely related to pore size) as well as components that are non Kelvin-like (pore size independent). These relationships are [5]:

$$K_0 \quad \frac{\delta_0}{h} - \varepsilon_0 \qquad (1)$$

$$K_1 \quad \frac{\delta_1}{h} - \varepsilon_1 \qquad (2)$$

where *h* is pore size in nanometers. Data fitting has yielded values for the parameters in (1) and (2), given as: δ_0 , δ_1 , ε_1 and ε_0 for rigid carbon networks at a temperature of 303 K [5].

Additionally, after contrasting data for water bound between non-rigid graphene layers which indicate Kelvin-like condensation features [5] with rigid carbon networks that do not display Kelvin-like behavior, the following general proposal was made for water in carbon [5]:

$$ln\left(\frac{1}{K_0}\right) \quad -\frac{2\sigma cos\theta_0 v_M}{R_g T h} \quad \varepsilon_0 \qquad (3)$$

$$ln\left(\frac{1}{K_1}\right) \quad ln\ a_{POI} \quad -\frac{2\sigma cos\theta_1 v_M}{R_g T h} \quad \varepsilon_1 \qquad (4)$$

where θ_0 and θ_1 are the contact angles of primary and secondary site water with the flat surface plane. Bulk fluid properties are included and σ represents the surface tension for water (σ=72 mN/m) and v_M represents molar volume of water (18 cc/mol for water). Additionally, R_g is the universal gas constant and *T* is absolute temperature.

3.1 REPRODUCIBILITY OF THE PROPOSED RELATIONS

Although the analysis presented herein is applied to a small data set, a concurrent study has vetted Equations (1) and (2) by analysis of 15 critically selected isotherms for water in non-functionalized carbons with narrow pore size distribution (PSD) [14]. The concurrent study aims to establish the utility of IMA to represent isotherms in a fashion consistent with other analyses but does not offer elucidation of mechanisms. Importantly, the concurrent vetting ensures that Equations (1) and (2) provide a valid starting point for this study to elucidate mechanisms and to allow physical interpretation at the macroscopic level.

3.2 INTERPRETATION OF THE PARAMETER ε

The parameter ε has been shown to be a discriminating parameter that is capable of distinguishing Kelvin-like from non-Kelvin like behavior [5]. The interpretation of ε_0 and ε_1 is evident at the large pore limit of Equations (3) and (4) given as:

$$\lim_{h\to\infty} ln\left(\frac{1}{K_0}\right) = \varepsilon_0 \qquad (5)$$

.

$$\lim_{h\to\infty} ln\left(\frac{1}{K_1}\right) = \varepsilon_1 \qquad (6)$$

It is apparent that the parameters ε_0 and ε_1 represent the primary and secondary site interaction, respectively, of water with the infinite pore surface. Interaction of water with solid surfaces can be attributed to surface wetting [15] with $\varepsilon_0 = 12.6$ representing primary site wetting and $\varepsilon_1 = 0.74$ representing secondary site wetting. To interpret these values it is necessary to calculate the net energy for nanoscale wetting which can be evaluated by the product of $\varepsilon_0 R_g T$ to yield the primary site surface wetting energy given as 31.2 kJ/mol. The product $\varepsilon_1 R_g T$ yields the secondary site surface wetting energy which is evaluated at 1.8 kJ/mol.

To assess these energies it is necessary to compare with isosteric heat of adsorption which is often reported in adsorption studies and is calculated as the difference from the heat of condensation. To calculate the heat of condensation the following relation is employed [16]:

$$\Delta H_c = -A\left(1 - \frac{T}{T_c}\right)^n \qquad (7)$$

with A=52.053 kJ/mol, T_c = 647.13 K and n = 0.321. At 298 K, the estimate is ΔH_c = -42.7 kJ/mol. Using this estimate for the heat of condensation, isosteric heat for primary sites is calculated at q_{st0} = 11.5 kJ/mol and for secondary sites is estimated at q_{st1} = 40.9 kJ/mol. These values are presented in Table 1.

System	q_{st0} (kJ/mol)	q_{st1} (kJ/mol)
IMA of carbon networks [5]	11.5	40.9
Ulberg and Gubbins [10]	4-12	30-40
Striolo et al.[11]	6-14	50-60
Birkett and Do [17]	6.82-14.58	N/A
Nguyen and Bhatia [18]	5-10	35-46

Table 1: Isosteric heats of adsorption for water-surface interaction q_{st0} and water-water-surface interaction q_{st1} on non-functionalized carbons.

The mechanisms associated with the Ising model suggest that the interaction of water with primary sites should be representative of fluid-solid interaction. Likewise secondary site interaction of water should be governed by fluid-fluid and fluid-solid interaction. Therefore, consistency with the Ising model dictates that the values of isosteric heat should be indicative of these interaction energies. For validation of this proposal, it is necessary to compare with molecular simulation estimates of isosteric heat.

3.3 VALIDATION OF NANOWETTING PARAMETER (ε) WITH ISOSTERIC HEAT

Molecular simulations of water in non-functionalized carbons have been undertaken in order to understand water-carbon and water-water-carbon interactions. Table 1 contains the isosteric heats calculated by molecular simulations using different potential models, some of which estimate higher values for the heat of vaporization of water. However, two important results are evident from simulation. Firstly, fluid-solid interactions are prevalent at low loading and the isosteric heat ranges from 4 to 14 kJ/mol. At higher loading, fluid-fluid interactions are introduced and can dominate fluid-solid due to the higher interaction energy. This energy is near that for vaporization and can range from 30 to 50 kJ/mol. Importantly, the mechanisms of the Ising model and the analysis results presented herein are both compatible with these simulation results. This can be seen in Table 1, and the agreement adds validation to the assessment of nanowetting. In order to validate the assessment of nanocapillarity, pore heterogeneity should be addressed.

3.4 EFFECT OF PORE HETEROGENEITY ON AFFINITY

Recently, Yang et al. [19] studied water behavior between graphene layers in a non-rigid system showing approximate agreement with the Kelvin relation down to 0.4 nm spacings as well as contact angles indicative of a continuum level condensation process. However, in rigid carbon networks that do not allow relaxation, effects of pore size variability would need to be considered. Even for ideal materials with little variation in pore size, the effect of PSD appears to be significant on the isotherm shape as noted by Nguyen and Bhatia [18].

Effects of PSD can be understood by consideration of Equations (1) and (2) which indicate that pore size does not influence the infinite surface wetting parameters ε_0 and ε_1. Additionally, although the values of δ_0 and δ_1 were determined by assessment of carbons with narrow PSD, a

pore heterogeneity factor denoted as r_0 is introduced into the analysis to account for finite range of pore size. This factor is treated as a constant that is averaged across the data set and additionally could absorb other forms of pore heterogeneity possibly in the form of asperity manifested in Wenzel roughness. Importantly, pore heterogeneity affects the parameters δ_0 and δ_1 and therefore estimates of contact angles. To ignore this effect could lead to false estimates of contact angle.

Furthermore, although the true functional form of the pore size distribution is unknown and the result averaged, the methods proposed herein and discussed in later sections, allow for direct evaluation of pore heterogeneity factor r_0. Therefore, the influence of heterogeneity can be parsed from the determination of contact angle.

3.5 WATER ADSORPTION MODEL USING MODIFIED KELVIN ANALYSIS

Analysis of the wetting behavior indicates that there are two modes of water interaction with carbon. One is primary site adsorption which is governed by solid-fluid interaction and the other is secondary site adsorption which additionally incorporates fluid-fluid interaction. This is in accordance with the Ising model and molecular simulation. For clarity, these modes are represented as Mode 0 for primary site and Mode 1 for secondary site interaction and they have the following features:

Mode 0 (Primary site interaction of water with the surface allowing nucleation of water clusters): Surface interaction (wetting/adhesion), referred to herein as primary site surface wetting, is significant in this mode. As a result of adhesion, a very low contact angle is expected. According to several studies [20,21], the surface interaction energies observed herein should yield zero contact angle. Hence, the contact angle for primary site bonding is assigned a nil value ie. $\theta_0 = 0$.

Mode 1 (Secondary site, cooperative, clustering interaction of water molecules with Mode 0 adsorbed water): This is dominant at moderate to high humidities or relative pressures where the isotherm upturns due to cooperativity and hydrogen bonding. Fluid-fluid interactions are significant in addition to fluid-solid interactions and contact angles indicative of bulk values on carbon surfaces are observed [19].

With the pairing of these Modes and the inclusion of capillarity and wetting at the nanometer level, the relations can be constructed as modified Kelvin analysis (MKA). MKA can be expressed be rewriting (3) and (4) to include effects of pore heterogeneity and the assertions above for Mode 0 and 1 as:

$$ln\left(\frac{1}{K_0}\right) = -\frac{2r_0\sigma v_M}{R_g T h} + 12.6 \qquad (8)$$

where r_0 is the pore heterogenity factor and

$$ln\left(\frac{1}{K_1}\right) = ln(a_{POI}) = -\frac{2r_0\sigma cos\theta_1 v_M}{R_g T h} + 0.74 \qquad (9)$$

where θ_1 is the angle of secondary site associating water (Mode 1) with the flat surface. Using bulk fluid properties of water (surface tension σ=72 mN/m and v_M=18 cc/mol), the only variable in MKA of Equation (8) is the pore heterogeneity factor r_0. This can be evaluated by application of Equation (8) to measured data and deployed in Equation (9) to estimate contact angle. Hence MKA can separately determine pore heterogeneity and decouple it from the estimation of contact angle.

3.6 EVALUATION OF PORE HETEROGENEITY FACTOR

In a previous study [5], the Ising model was applied to generate values for Henry's law constant K_0 and secondary site affinity K_1. Figure 1 shows the value of K_0 against pore half width together with the fit of equation (8) for bounding values of the pore heterogeneity factor r_0 at 3.4 and 3.8. Some variability is evident (roughly 15%) for this factor which performs reasonably well at characterizing this form of pore heterogeneity.

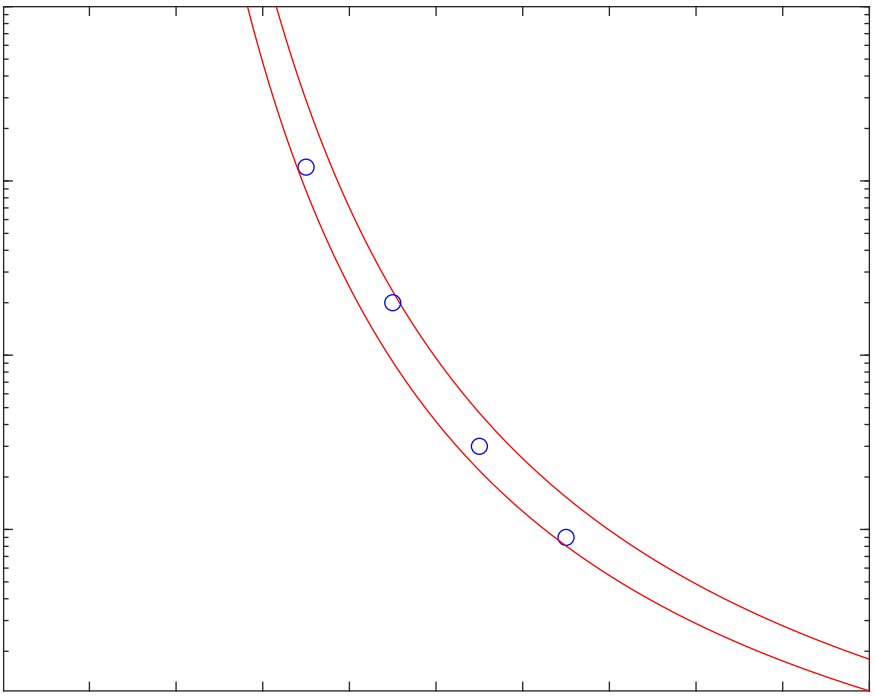

Figure 1: K_o as a function of pore half width for a series of ACF as determined in a previous study at 303K [5]. The pore heterogeneity factor values that bound the data are 3.4 and 3.8.

3.7 EVALUATION OF CONTACT ANGLE

Having bounded the pore heterogeneity factor r_0, an averaged value is employed in Equation (9) to evaluate contact angle. A previous study has obtained estimates of K_1 and also shown that it is related to the relative pressure at the POI: $a_{POI} = \frac{1}{K_1}$ [5].

Figure 1 presents a_{POI} plotted against pore half width, h in nanometers. The prediction of Equation (9) is shown for two values of contact angle that bound the data at 80.5 to 81.5º. Notably, this overlaps with the contact angle observed by Kozbial et al. [22] who found the water contact angle of aged flat CVD graphene was 81.2 ± 1.4°.

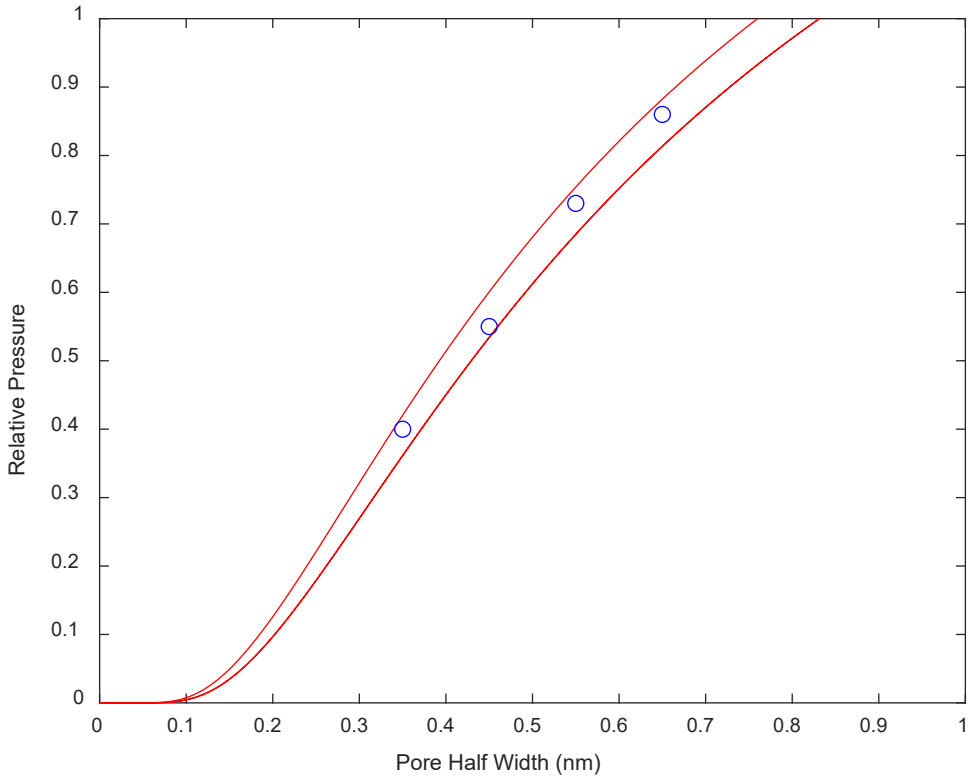

Figure 2: Relative pressure at POI (a_{POI}) as a function of pore half width for a series of ACF as determined in a previous study at 303K [5]. The contact angles bounding the data are 80.5 to 81.5 degrees.

3.8 REEVALUATION OF CONTACT ANGLE OF WATER BETWEEN GRAPHENE LAYERS

The contact angle for water between graphene layers has been studied by Yang et al. [19] under the proposal of no surface wetting and Kelvin-like behavior. By regression analysis, this was shown to be a reasonable proposal [5]. However, molecular simulations by Faraji et al. [23] suggest that the work of adhesion is not zero and that simulations with the inclusion of adhesion can characterize the data. To resolve this, this study has re-assessed the data of Yang et al. [19]. Using Equation (4) with bulk properties of water and the assumption of no wetting ($\varepsilon_1 = 0$), contact angles between 81 and 88° successfully bound the data as shown in Figure 3.

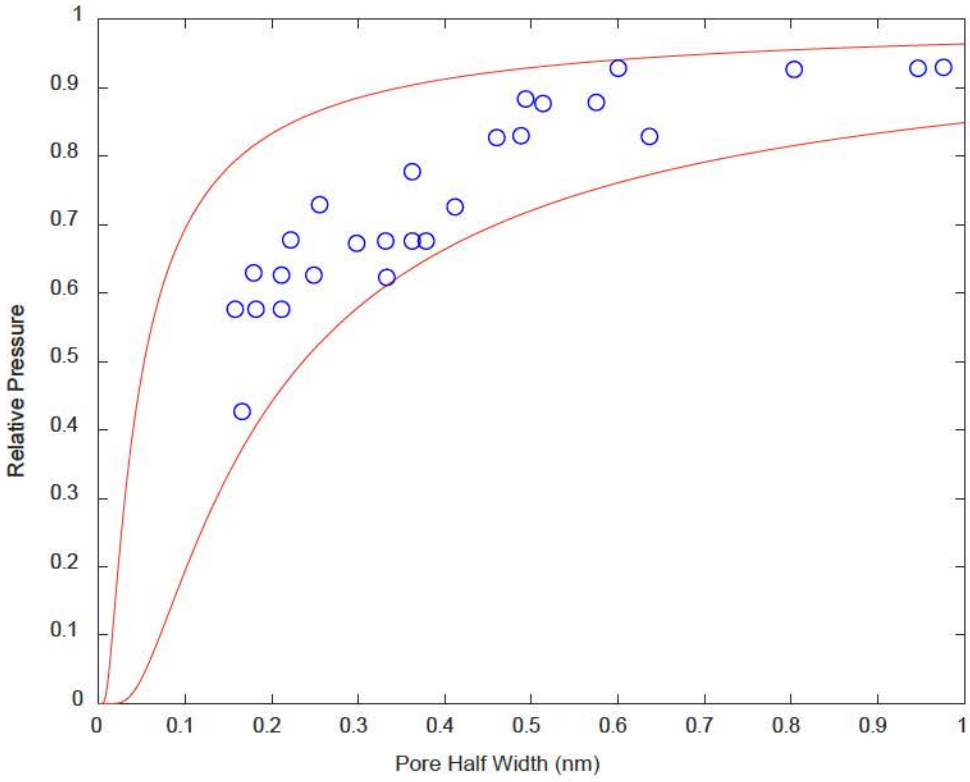

Figure 3: Data of Yang et . [19] at 294 K showing contact angles between 81 and 88° bound the data set

However, allowing for adhesion as suggested by Faraji et al. [23], ε_1 is adjusted to 0.1 and the result is shown in Figure 4. Although only a small amount of adhesion is involved in the adjustment, the data set is better described by this proposal in the respect that the bounds of contact angle are reduced. These angles are presented in Table 2 and it is noted that they are near the historically used values for pure water and graphite surface which was measured by Fowkes et al. [24] at 85.3 to 85.9°. Additionally, other experimental studies have assessed the contact angle to have high variability and when measurements are pooled and collectively assessed, the estimate appears to be 89 $\pm$10° [25] for graphite. Agreement for the values assessed in this study with other values is indicated in Table 2.

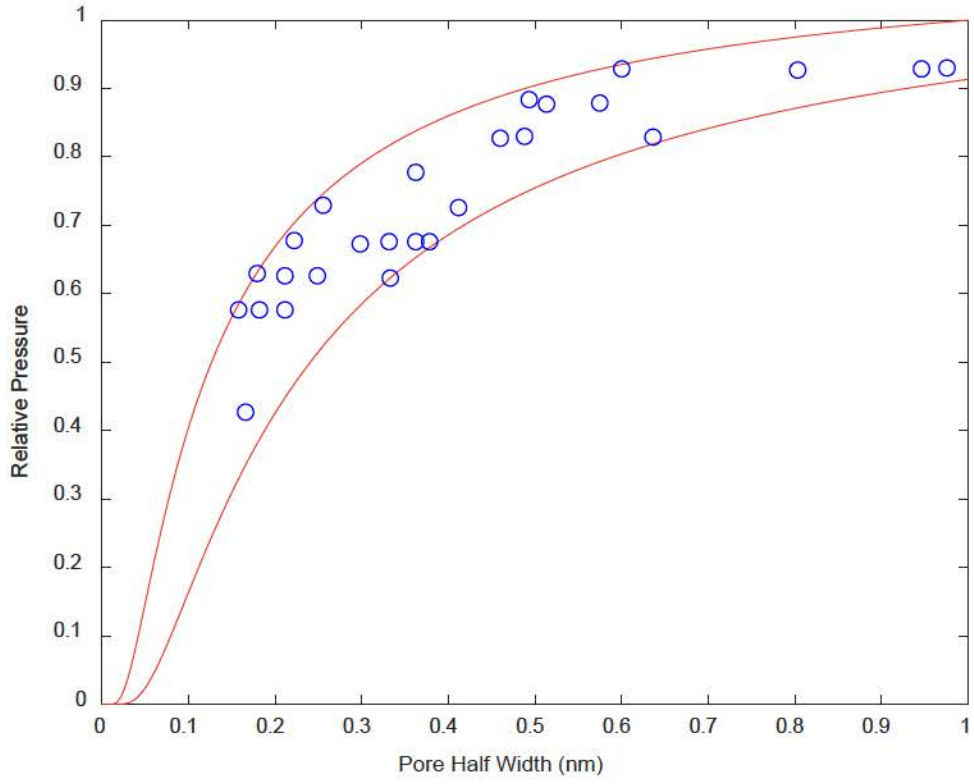

Figure 4: Data of Yang et al. [19] showing contact angles of 82 $\pm$2° and ε_1=0.1 bound the data

System	θ_1	Reference
Carbon Networks (data assessment)	80.5 to 81.5°	This work
Aged Graphene via CVD (measured)	81.2 ± 1.4°	Kozbial et al. [22]
Graphene layers (data assessment)	82 ±2°	Yang et al. [19] and this work
Aged Graphite (data assessment)	89 ±10°	Carlson et al. [25]
Graphite (measured)	85.3 to 85.9°	Fowkes et al. [24]

Table 2: Assessed contact angle or water in graphite/graphene systems

Importantly, comparison of contact angles demonstrates that the methodology proposed herein allows for successful estimation of a macroscopic, continuum property from a nanoscale system. Additionally, this result could be employed not only to characterize contact angle at the nanometer level but also to predict adsorption isotherms for carbon networks with known pore size. It is also foreseeable that this result could also be applied to characterize heterogeneous materials with broad PSD, thus making it a potentially valuable tool for characterization of microporous solids.

4.0 CONCLUSION

Results obtained through employment of IMA and used to establish relationships with pore size are interpreted by consideration of solid-fluid and additional fluid-fluid interactions. The analysis applied in this study indicates that a Kelvin relation modified for surface wetting appears to be valid for use at the molecular level. The resulting Ising Model- Modified Kelvin Analysis (IMMKA) addresses heterogeneity presented by real materials and is able to successfully characterize and assess this heterogeneity. Furthermore, IMMKA allows contact angles to be successfully estimated via the methodology proposed in this investigation. Values of contact

angle similar to those seen for water in other carbons systems are successfully characterized. Additionally, isosteric heats extracted from the model are also comparable with molecular simulation results. Furthermore, the favorable comparison of contact angles, isosteric heat and isotherm features lends validity to the IMMKA model which can successfully elucidate mechanisms and interpret structural features of the system at the nanometer level. Importantly, it simultaneously allows macroscopic fluid properties to be used to understand water adsorption in micropores.

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