Using classical methods to start quantum mechanical calculations for microporosity and mesoporosity

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Abstract

One primary measurement of open porosity uses physical adsorption isotherm, amount adsorbed versus gas pressure. Classical treatments, including the BET, cannot fit the isotherm for its full range, therefore standard curves have been created from non-porous materials for comparison. This classical method yields three output parameters, two surface areas, pore and external, relative to the standard. The third output is moles of material needed to fill the pores. A modern treatment using quantum mechanics and thermodynamics, call χ/ESW, yields seven physical quantities. However, the calculation requires a non-linear least squares routine, with initial parameters to find a minimum. In this paper the possibility of using the answers from the classical method as a first approximation is explored, with no need for a standard since χ/ESW treatment is used as a self-standard. Within limits, this works well for microporosity but mesoporosity presents some problems with one of the parameters.

Keywords Microporosity · Mesoporosity · Adsorption · Physical-adsorption · Quantum-mechanical-modeling · Physisorption

1 Introduction

One of the major measurements of physical adsorption is the adsorption isotherm, that is, the dependence of amount adsorbed as a function of pressure. The dependence is usually described by the generalized equation:

$$\theta = \mathbf{F}(P, T) \tag{1}$$

θ is usually the "coverage," defined as the number of moles of molecules adsorbed on the surface, n_{ads} called the adsorbate, divided by a quantity that is a monolayer equivalent, n_m. The quantity n_m is defined as the moles of adsorbate molecules that are needed to completely cover the surface if they were all in direct contact with the surface. P is the pressure of the gas, called the adsorptive, that is, the source for the adsorbate. The solid material upon which adsorption occurs is called the adsorbent. For the isotherm, T is supposed to be held constant and the isotherm is dependent only upon P.

Before 1980, theories for determining porosity were by themselves not very successful. Thus, the use of standard curves was proposed, first by deBoer (deBoer et al. (1965)), et. al. and by Cranston and Inkley (Carnston and Inkley 1957) and later by Sing (Bhambhani et al. 1972; Sing et al. 1974), and the latest IUPAC recommendations (Thommes et al. 2015). Unfortunately, the deBoer t-curve was not consistent with later data and it has been speculated that the sample temperature control was problematic. The Sing's, et. al., α-s curves are still used today, especially for silica materials. There are many other standard curves for other adsorbents in the literature.

The methodology, which will be referred to here is the classical treatment, was to plot the amount adsorbed versus the value of the α-s curve. α-s curve is the data from a non-porous sample whose chemistry is similar to the porous sample of interest. For non-porous silica samples, this plot should obviously be a straight line, the slope of which is proportional to the surface area. For porous samples this plot deviates from a straight line. For a microporous sample, the plot produced is similar to that shown in Fig. 1. Figure 1 is an idealized form of an isotherm seen with a microporous sample.

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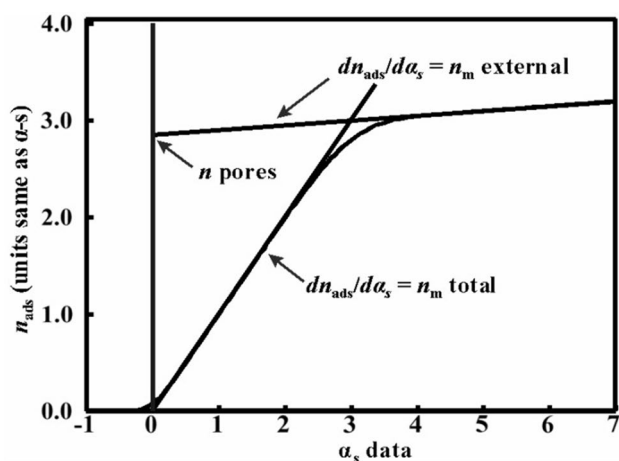1   Roane State Community College, Harriman, TN, USA

Fig. 1 The model isotherm of a microporous silica sample

The features of this plot are:

1. a low-pressure linear portion
2. a portion that has a negative curvature and
3. a high-pressure linear portion

These features are interpreted in the following fashion:

1. a straight line is fitted to the low-pressure region and
2. another straight line is fitted to the high-pressure region.
3. the high-pressure straight line is extrapolated to the ordinate axis.[1]

These three features are interpreted respectively as:

1. a value that is proportional to the surface area of pores plus the external area, n_m, that is, the total surface area.
2. a value that is proportional to the surface area of the external area, $n_{m,ext}$.
3. the n value on the ordinate is the number of moles to completely fill the pore volume, n_p. (The opposite extrapolation of the "Gurvich" rule (Gurvich 1915)).

There does not appear to be any flaw in the reasoning for the interpretation of these physical quantities, which is based on simple intuitive reasoning. Unfortunately, the surface areas of the standards cannot be determined with the usual classical treatment, that is, using the BET theory. Since, until recently, most DFT calculations depended upon the BET for surface area to start the calculation, its use presented problems in the analysis, and attempts to avoid the

BET, have not been successful. For example, in attempts to use DFT only for the early part of the isotherm resulted in undulations (Landers et al. 2013).

It is now known that there are a few more parameters can be obtained from experiments. A total of seven output parameters are possible with good experimental data. A similar diagram can be drawn for mesoporosity and the same output parameters are obtained.

The χ/ESW treatment in analyzing these isotherms yields these parameters and much more information with a greater degree of certainty.

2 The quantum mechanical interpretation—background

In previous publications, which are summarized in a book (Condon 2020) written as an introductory textbook for graduate students, simple methods were presented as to how to measure the monolayer equivalence, n_m, (related to surface area), the micropores and the mesopores of solids by physical adsorption. The output parameters of interest in these investigations should include:

1. n_m total monolayer equivalents, that is, for the area inside the pores and external to the pores.
2. the energy of first molecule adsorbed, E_a, obtained by an output parameter χ_c
3. the moles adsorbate that fill mesopore or micropores, n_p
4. the final $n_{m,ext}$ after pore filling, that is for the external surface
5. the numbers of complete, or partial, "monolayers" that are in the pores obtained by the parameter $\Delta\chi_p$
6. the energy distribution for a heterogeneous surface, σ_c, and
7. the distribution in $\Delta\chi_p$, σ_p.

These parameters are directly related to all the surface areas, external and pore, the pore volume, pore size, the adsorption energy, and possibly pore shape.

All of these properties may be obtained from the χ-plot. This plot is based on the χ and ESW hypotheses, which in turn are based on quantum mechanical perturbation theory and thermodynamics respectively. The theoretical treatment was developed by two research groups working independently in Oak Ridge (Condon 1988a, b; Fuller and Condon 1989) and Germany (Adolphs and Setzer 1996, 1998; Churaev et al. 2000; Adophs 2007). The Oak Ridge group named the treatment χ (chi) for the quantum mechanical

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[1] This is a modification of Gurvich rule in this publication given with the insight of χ/ESW.

treatment or Auto Shielding Physisorption (ASP)[2] for the classical explanation. The German group referred to their thermodynamic treatment as "Disjoining Pressure Theory of Physical Adsorption" and later called it "Excess Surface Work" or ESW. The theoretical derivation takes more space than allowed here but a complete derivation for both approaches is available in reference (Condon 2020). The resulting equation, however, is quite simple and it relates the surface coverage, ($\theta = n_{ads}/n_m$) to the quantity χ ($\chi = -- \ln (- \ln(P/P_{vap}) > 0)$) by:

$$\theta = (\chi - \chi_c)\, \mathbf{U}(\chi - \chi_c) \tag{2}$$

The symbolism $\Delta\chi = \chi — \chi_c$ for convenience will be used. The constant χ_c is defined as the value of χ as:

$$\lim_{n \to 0}(\chi) = \chi_c \tag{3}$$

Equation 3 is required by the QM perturbation theory, QM/KBW approximation (Condon 2000a,2000b) and thermodynamics (ESW.) This implies that there should be a finite pressure as the adsorbate approaches zero. This has been observed by several investigators. It implies the start of a phase change.

Equation 2 has been known to be an excellent fit to the isotherm first noticed by deBoer and Zwitter (deBoder and Zwikker 1929). At the time this isotherm was highly debated and unjustly criticized for the wrong reasons. However, as the title of their article indicates, it missed the real reason that the equation worked. (To be fair, quantum mechanics was in its infancy at the time and little likelihood that they would have made any connection.)

The function **U** is the unit step function, which simply says that the value of θ cannot be less than $\theta = 0$. Since mathematically, $P > 0$ even if $\theta = 0$, then these equations are in direct conflict with most other descriptions of physical adsorption. Specially they predict "Henry's law" is not valid for physical adsorption.[3] The need for and observation of a finite positive value for $\Delta\chi = \chi - \chi_c$ disproves soundly all "Henry's Law" physical adsorption theories, one of which is the BET.

From Eq. 2, χ_c and thermodynamics, one can calculate all those items listed above. Furthermore, the heat of adsorption can be calculated as a function of temperature and pressure from this equation using nothing other than one isotherm. Given the proper conversion factors one can calculate the following properties for space and energy:

1. The initial n_m yields total specific surface area
2. E_a (< 0 by convention) and thermodynamic relationships yield the heats of adsorption as a function of θ, $\mathbf{E}(n_{ads}.)$
3. n_p yields the pore volume.
4. $n_{m,ext}$ yields the final external surface area.
5. $\Delta\chi_p$ yields the pore radius for micropores and $r_p - r_{core}$ at prefilling for mesopores.
6. A distribution in χ_c yields a distribution in E_a (a measure that is impossible with other theories.)
7. A distribution in $\Delta\chi_p$ ($= \chi - \chi_p$) yields a distribution in pore radii.

The observation of Eqs. 2 and 3 has been observed on nonporous standards (Condon 2001) and predictive of later observations (Gammage et al. 1970,1974; Fuller and Agron 1976; Fuller 1976,1982; Fuller et al. 1984). These equations have also been observed at low pressures with porous samples (Condon 2002a). The disproving phenomenon called the "threshold pressure" has been addressed and confirmed specifically (Fuller and Agron 1976; Fuller 1976) (Condon 2020).[4] These observations also support the conclusion that the BET, and similar theories are disproved. The reason that these type observations are not commonly reported is the lack of low-pressure data.

It has also been demonstrated that with a single isotherm one can predict the energy of adsorption as a function of n_{ads} without any additional parameters. Thus, the measurement of n_{ads} as a function of adsorbing gas pressure, P, from a single isotherm can predict the energy of adsorption without any additional input information. These energy values thus obtained are in excellent agreement with calorimetric measurements (Condon 2002b).

The microporosity and mesoporosity[5] calculation using χ appear to have been successful, but there is always a problem finding appropriate experiments to completely check the calculations. One problem is that the observations for the pore distribution[6] is tied up with the heterogeneity of the surface. In other words, if there is a distribution of E_as, this distribution carries over and adds to the observation of the distribution for the pores. The standard deviation for observed σ_2 at the negative curvature for the pores is a combination σ_c,

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[2] The QM treatment preceded the ASP but was difficult to get published, whereas the ASP seem more classical and was somewhat acceptable, but theoretically incorrect.

[3] This is NOT the original Henry's law which applies to solutions! The extrapolation from 0.05 P/P_{vap} used simply because some researchers could not measure in low (UHV) pressures. It is in no way mathematically or thermodynamically related.

[4] See Chapter 5 section "Thompson" (The publications of these experiments were rejected by multiple journals.).

[5] Defined here as micropores: adsorption in pores without the surface tension effect to fill the pores in any way except by continued surface adsorption and mesopores: partially filling the pores by surface adsorption and the quickly finish by the tensile strength of the outer interface formation.

[6] The pore distribution observation is tied up with the filling of "layers." The quotes indicate that the definition of layers is different from the normal layer-by-layer description. Some hint of the meaning here is given below in **Case B**.

for the energy, and σ_p, for the pore distribution. They are related by:

$$\sigma_2^2 = \sigma_c^2 + \sigma_p^2 \tag{4}$$

assuming no correlation. Thus, to obtain σ_p one needs to measure σ_c. It is very rare for researchers to measure in a pressure range low enough to measure E_a much less with enough accuracy to obtain σ_c.

There is a further complication which will be addressed in this publication, that is, if σ_c and σ_2 overlap then the measurement of n_m will be incorrectly measured low. Another equation may be derived from derived from Eq. (2) to take into account distributions in E_a and the σ_p, which includes both mesopores and micropores. This is:

$$\theta = n_m \mathbf{Z}\big(\chi, \langle \chi_c \rangle, \sigma_c\big) + (n_{m,ext} - n_m)\mathbf{Z}\big(\chi, \langle \chi_p \rangle, \sigma_2\big) + \big[n_{meso}\mathbf{D}(\chi, \langle \Delta\chi_p \rangle, \sigma_2) \text{ if : } n_{meso} \geq 0\big] \tag{5}$$

with "<>" here indicating the mean value. The n_{meso} is defined as the moles needed to fill the pore minus the moles originally on the surface at the point at which the prefilling begins. In other words: $n_{meso} = n_p - n_m + n_{m,ext}$. at the start of prefilling.

Both the functions $\mathbf{Z}$ and $\mathbf{D}$ are given by:

$$\mathbf{Z}(x,y,z) := \int_{-\infty}^{\chi} \mathbf{D}(x,y,z)dx, \quad \int_{-\infty}^{\chi} \mathbf{D}(x,y,z)dx = (x-y)\,\mathbf{D}\,(x,y,z) + z^2\mathbf{G}(x,y,z)$$

$$\mathbf{D} = \int_{-\infty}^{\chi} \mathbf{G}(x,y,z)dx \quad \text{and} \quad \mathbf{G}(x,y,z) := \exp\left(\frac{-(x-y)^2}{2z^2}\right) \tag{6}$$

This might look complex, but the functions $\mathbf{G}$ and $\mathbf{D}$ are functions available in most spreadsheets as the "Gausian" or "normal" distribution, and the "normal cumulative" distribution. Distributions other than the $\mathbf{G}$ could be used, but until now there has been little justification for this. For micropores only the first two terms on the right of Eq. (5) apply. The third term expresses the prefilling which includes the surface area coverage and therefore the second term remains even though the filling is not in micropores. In practice, so far, the second and third term of Eq. (5) have had the same $\langle \Delta\chi_p \rangle$ and σ_2, indicating the samples did not have a mix of micropores and mesopores. There is no reason that there cannot be such a mix. This would complicate the situation with additional terms. Furthermore, there is no reason to assume that the normal distribution should always be used. However, in practice no data set has been found where a higher refinement is justified due to data scatter.

3 Previous calculations

3.1 Previous ESW calculations

This paper is written from the χ approach to the problem of isotherm analysis. The thermodynamic ESW approach can be connected to χ with the realization that the disjoining pressure, $\mathbf{H}(h)$, as a function of film thickness, h, and energy of adsorption are related by:

$$\overline{V}\mathbf{H}(h) = \overline{E}_{ads}(\Delta\chi) \text{ and } \overline{V}H_0 = \overline{E}_a \tag{7}$$

The over-bars are to indicate per mole quantities. See reference (Condon 2020) chapter 4 (section "The disjoining pressure derivation, (ESW)") for complete derivation and explanation.

The some early mesopore modeling used what was referred to as the "DBdB theory", which is a combination of disjoining pressure theory by Derjaguin (1941, 1957) and Broekhoff and deBoer theory (1967)[7] of small capillary filling. More recently the DBdB theory has been combined with the modern understanding of the application of ESW, to do calculation on porosity as well as surface area (Churaev et al. 2000; Georgi et al. 2017; Kolesnikov et al. 2017).

3.2 Previous χ calculations

Equation 5 has been used to calculate both micropores and mesopores. Performing a least-squares fit to data is a tedious process without some initial estimates. Nevertheless, this was done with the data by Danner and Wenzl (Danner and Wenzel 1969) (DW), Goldmann and Polagni (Goldmann and Polanyi 1928) and Wisniewcki and Wojsz (Wisneiwshi and Wojsz 1992) for microporosity. For microporosity, the starting parameters from the classical analysis were reasonably close to the final answer to avoid false minima. For mesoporosity, however, this was a bit more difficult and some visual

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[7] Note of caution: In this reference Eq. 14 is missing a γ on the left side. Equation 13 is OK.

Table 1 Statistics of the calculation

Danner and Wenze (1969)				Qiao et al. (2003) N_2 adsorption			
Type:	R^2	σ fit relative to full range	Error of slope $/n_m$	Type:	R^2	σ fit relative to full range	Error of slope $/n_m$
10X-O2	0.995	1.13%	− 1.95%	MCM-41 C10	0.996	0.76%	5.5%
10X-N2	0.996	1.36%	0.08%	MCM-41 C12	0.997	0.60%	4.0%
10X-CO	0.997	1.44%	2.47%	MCM-41 C14	0.997	0.55%	3.6%
5A-O2	0.998	0.82%	0.11%	MCM-41 C16	0.984	1.08%	− 2.0%
5A-N2	0.992	1.98%	0.08%	MCM-41 C18	0.998	0.36%	3.0%
5A-CO	0.996	1.43%	0.31%	MCM-41 C22	0.994	0.49%	2.5%

guidance was required to allow the program to find the best minimum. Obvious false minima were often obtained. Never-the-less the fit was performed (Condon 2002c) for the data by Qiao, Bhatia and Zhao (Qiao et al. 2003) (QBZ) and Kruk and Jaroniac (Kruk and Jaroniec 2001). In all these cases the final fits were very good and the output parameters made sense. However, with the exception of QBZ data, there is no way to compare the answer with other methods. The QBZ data, being the exception, also measured the pore radii with X-ray analysis. The wall thickness, which surround the pores, was calculated to be 0.63 to 0.94 nm with a standard deviation of 0.17 nm including outliers. These values are in reasonable agreement with expectation. In Table 1 are some statistics for the fits to the data by DW and by QBC. The statistics clearly shows that use of Eq. (5) yields very good fits to experimental data.

The routines used to make the calculations were simple minimum search routines. The problem with this approach is if the initial estimates are not close to the final answer, then a false local minimum could be approached. There are two ways to detect this problem. The first is to notice that the standard deviation of the fit is very high, much higher than the data would indicate. The second is a visual inspection of the fit versus the data. Such problems require a re-estimate of the starting parameters and starting over. This may be the most time-consuming part of the solution, since even with most desktop computers the routine itself converges quickly.

However, if one tries to randomly select starting parameter estimates it may take considerable computer time and the calculation may converge to a false minimum. One method around this is to start with the classical estimates and setting σ_c and σ_2 to low values. The questions to be answered here is, "How good are the classical values? What approach, if there is one, could be better?".

4 Experimental:

The classical interpretation was used as a starting point for the calculation. One important difference is that the χ calculation provides an embedded "standard curve." The method

for determining the initial parameters for microporosity has been illustrated in Fig. 1 and the explanation above. A similar tactic is advised for mesopore analysis. Both analyses with classical parameters might be assume approximate. Once the classical parameters are determined, a fit to Eq. (5) using a computer routine is recommended for accuracy.

The question now becomes, "How good are the classical approximations?" Given the agreement between Eq. (5) and the data, this is an important question. How close do the recommended approximations, which use just the slopes of the early linear portion of the isotherm and the linear portion nearing P_{vap}, yield answers close to the true value. To do this one can construct "ideal" curves and check to determine if by inputting the values that would normally be determined from the fit of Eq. (5). If this is the case, how much and what kind of error one might expect?

4.1 Microporosity

In Fig. 2 are simulations of microporosity using Eqs. (5) and (6) for four different cases of parameters that would normally be outputs from the least-square fit. These parameters were the input to Eqs. (5) and (6) to determine how close would one be able to retrieve these parameters by the classical technique. The important features and consequences are:

4.1.1 In case A

There is little overlap in the distributions and the value for $<\Delta\chi_p>$ is very close to the input value, the number given. Even a small $<\Delta\chi_p>$ could work with a small distribution in E_a (σ_p).

4.1.2 In case B

Not surprisingly, the more the overlap of the E_a distribution and the $\Delta\chi_p$ distribution is, the worse the estimate of $<\Delta\chi_p>$. This happens when the separation between E_a and $<\Delta\chi_p>$ is small and a wide distribution for both exists as illustrated in case B. Such a wide distribution in E_a is unlikely for homogeneous material. Perhaps for doped
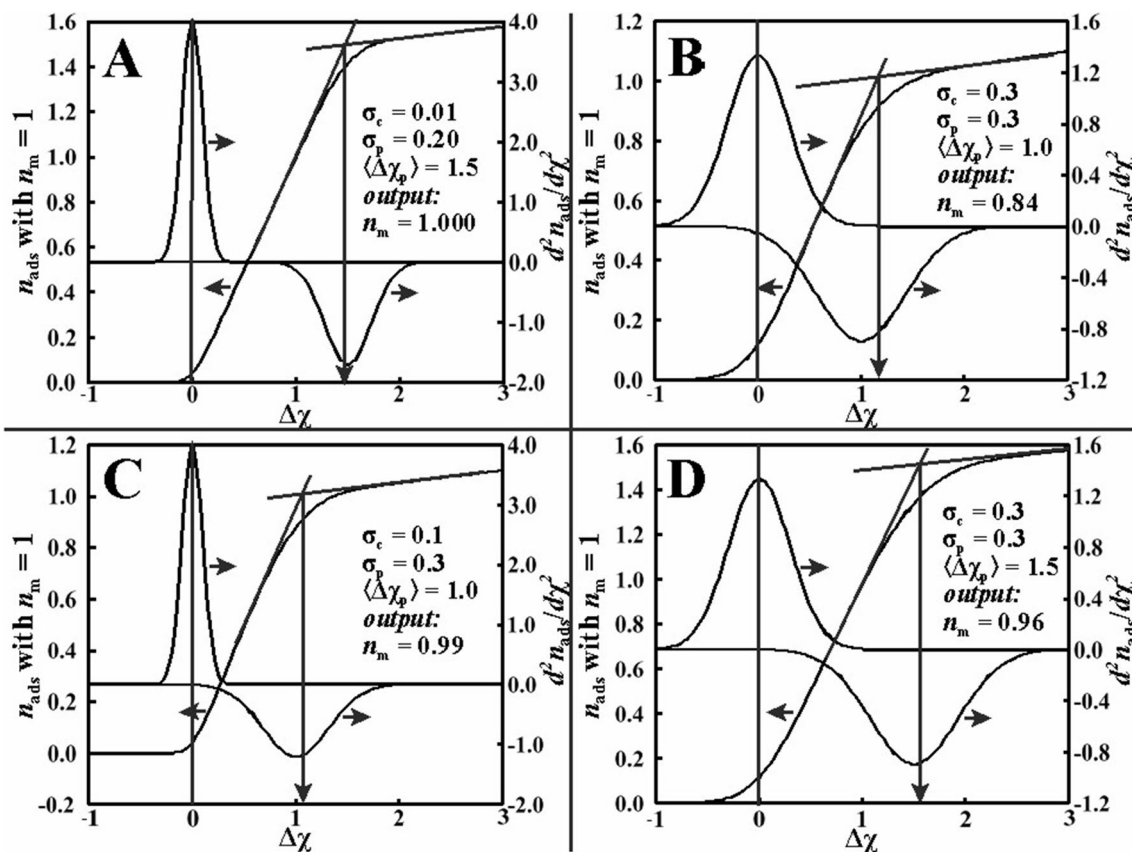
Fig. 2 Simulations of micropore materials with various heterogeneities in energy and pore sizes and separations to determine the effect on the n_m (input as 1) measurement. Percent n_m in pores is 98%. and 2% in n_{ext}. Arrows indicate which axis relates to the curve. The Gausians shown are G_1 and $G_2 = G_3$

material with, for example promoters, this might not be the case. Notice, however that this particular case is limited to a monolayer thickness and can be better handled by an alternative method referred to as the log-law.

The log-law mentioned, is a special case of the "layering" in the derivation of the χ-plot equation. It should be noticed that since $\theta_{\text{bare adsorbent}} = \exp(-\Delta\chi)$ then $\theta_1 = 1 - \exp(-\Delta\chi)$ where the subscript indicates the "layer" in question.

This is iterated to yield the equation:

$$\theta_n = 1 - \exp\left(-\Delta\chi + \sum_{m=0}^{m=n-1} \theta_m\right) \quad \text{with } \theta_0 = 0 \left(\text{and} \Rightarrow \theta = \sum_{m=0}^{m=n-1} \theta_m \leq \Delta\chi\right) \tag{8}$$

which yields the value of each "layer." This is used to model when a physical barrier interrupts the normal "layer" filling by adding up the "layers," with the proviso that at some value of m the adsorption will be blocked. Such a barrier might be a pore wall. If it is interrupted at one "layer" thickness then $n = 1$ yields the log-law. See reference (Condon 2020) for details.) Thus, for θ_1:

$$n_{\text{ads}} = n_m\left(1 - \frac{RT}{E_a}\ln\left(\frac{P}{P_{\text{vap}}}\right)\right) \tag{9}$$

which is the log-law.

4.1.3 In case C

Case C illustrates that small overlaps have little effect on the classical analysis. In this case the distribution of E_a is sharp and the distribution in $\Delta\chi_p$ is wide.

4.1.4 In case D

For this case there are two wide distributions, but the value of χ_p is large enough that the overlap is small. Thus, a good
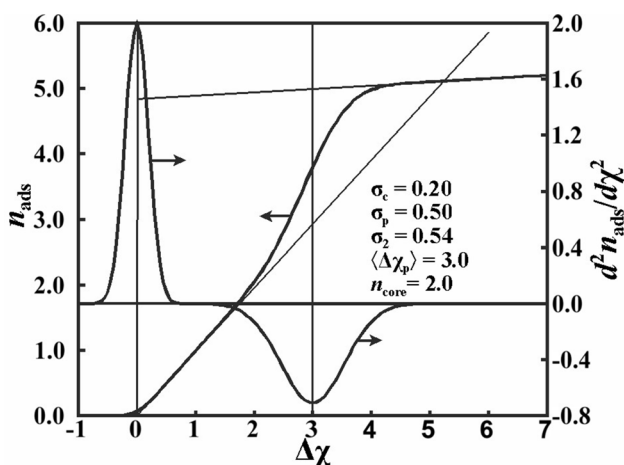
Fig. 3 The simulation of mesopore isotherm with the parameters given

estimate of $<\Delta\chi_p>$ can be accomplished with at least one sharp distribution or $<\Delta\chi_p> \geq 1.5$.

4.1.5 Correct n_m?

Looking at the resulting disturbances in n_m. The original n_m, which should be reflected by the first line slope, was set to 1.00 in the simulation. In case A the output for n_m is very good. For cases C and D the outputs are fairly close and could be a good starting point for the using the fitting routine. Case B, however is questionable. The calculation for n_m, however, is quite bad. In this case $n_m = 0.84$, 16% low. It is also the most difficult to fit a tangent to with real data. Even with this "perfect" isotherm the initial slope shows up more like an inflection point and not a straight portion. Data scatter with real data compounds the problem. This indicates that in the least squares fitting routine that n_m should be modified first. In general, if one were to use the classical method to determine the starting estimates for the output parameters for Eq. (5) with n_m as the lead-off parameter, it seems likely in most cases conversion will be rapid with little difficulty.

4.2 Mesoporosity

Turning to the mesopore case, a typical simulation for this is presented in Fig. 3. It seems that the prefilling starts at about $\Delta\chi \sim 3.0$, in other words, at a coverage of ~ 3 monolayer equivalents. This seems reasonable since, for this value, all the elements for a classical film are present—two fully formed interfaces and a separating interfacial fluid. The isotherm in Fig. 3 was generated using Eq. (5) with a finite n_{core} value.

The first thing to notice is that the straight-line extrapolation to determine the intersection is past the value of $<\Delta\chi_p>$

input value. There does not seem to be a classical method to approximate $<\Delta\chi_p>$. It is some place between the positive curvature around $\Delta\chi = 2$ and the following negative curvature. It would be incorrect to use the inflection point at approximately $<\Delta\chi_p> = 3.0$. This is due to the fact that both a Gausian (normal) and a cumulative distribution function are operational in this area. One of these functions has an inflection point at 3.0 but the other has a minimum. At any rate, with the presence of data scatter, this would be very difficult to do.

A suggestion to overcome this is to fit the isotherm with an arbitrary function, say an 8-power polynomial or some piece-wise function, and calculate the first and second derivative. This technique has several potential problems, one of which Eq. (5) has both a **Z** function and a **D** function. This yields a function of the form:

$$\frac{d^2\theta}{d^2\chi} = A\mathbf{G}_1 - B\mathbf{G}_2 + C\frac{d\mathbf{G}_2}{d\chi} \qquad (10)$$

Without the last term, this would yield the answers straight-forward. The terms $\mathbf{G}_1$ and $\mathbf{G}_2$ would yield a maximum and a minimum respectively needed for the values of $<\Delta\chi_p>$ and $<\Delta\chi_c>$ respectively. This works for micropores. However, the last term, needed for mesopores, muddles the analysis. For mesopores, other than a nonlinear least squares approach, there seems no easy way to approximate these parameters. Furthermore, most experimental data do not go below $<\Delta\chi_c> = 0$, so the full form of $\mathbf{Z}_1$ may not be obvious. Another problem is that high order polynomial fits have problems, some of which can be overcome by shifting the origin for the data.

Thus, it seems that, at least at this point, that one needs to make a guess as to the location of the position of the positive and negative curvatures and pick a starting value between them. It is always a good idea to check graphically what the fit looks like initially and after the detection of a minimum. False minima are plentiful for this, but they are also obviously false, so the need to restart with other starting parameters is clear.

5 Conclusions

The classical diagram, which is modified using χ-plot in place of standard plots based on other means can be used to approximate the values of the total surface area, the external surface area and the pore volume. For micropores it can also be used to approximate a quantity $<\Delta\chi_p>$, related to the pore diameter and shape. This value indicates the number of "layers" that can be inserted into pores, in a manner taking into account geometry.

For mesopores the diagram can be used for the total surface area, the external surface area and the pore volume, but not for $<\Delta\chi_p>$. At this time, it seems that the best estimate for $<\Delta\chi_p>$ is some point between the positive curvature for the start of mesoporosity increase and the finishing negative curvature for the leveling off for the pore filling. For mesopores, $<\Delta\chi_p>$ is obtained for the same reason that applies to micropores, that is, how many "layers" (on the average) form before the core of the pore prefills. However, obtaining this value is not as simple as with micropores.

These values calculated using classical reasoning are not the final answers, but rather a starting estimate for a minimal search routine for all seven fitting parameters. Graphical guidance is highly recommended due to the possibility of false minima.

After attempts to obtain starting estimate, using the full minimum least squares routine these isotherms can be analyzed. In both cases the $<\Delta\chi_p>$ yields a number for the surface area of the pores and the volume of the cores. With assumptions about geometry, this yields the pore radius. In addition, the χ-plot analysis yields the energies of adsorption as a function of coverage and the distributions of energy and pore size.

Compliance with ethical standards

Conflict of interest Not applicable.

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