

**Part V: Quantum Mechanics and Physisorption  
Microporosity**

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Title:

**Part V: Quantum Mechanics and Microporosity**

James B. Condon

**Abstract:**

In this part, the use of the log-law and the schicht equation will be demonstrated. These concepts are used for cases where the adsorption is sterically hindered so there is a premature cut-off of the “multilayered” adsorption either fully or in part. This could create a situation where one must keep several possibilities open. For example, the log-law might be followed for the hindered portion of the adsorption and the multilayer with a distinct heterogeneity, that is another  $E_a$ , for another portion of the isotherm might followed. Another possibility could be the steric hindrance restricted not to only the first schicht but also partially to the second.

These examples illustrate that the researcher cannot go automatic but have enough knowledge and skill to interpret the  $\chi$ -plot, the  $\Delta\chi$ -plot and the log-law plot and be able to set up a customized non-linear least squares routine for whatever combination of features are present.

When does one get it “right?” An arbitrary criterion that seems to exclude other fitting method has been advised. For very good data with very little obvious experimental scatter, a standard deviation for  $n_a$  of less than or equal to 1 % of the full range of the data (FRD) seems to be reasonable. This might be loosened a bit for mesoporosity and binary isotherms due to the difficulty of aligning the least squares routine with a rapidly changing value for the  $n_a$ s.

## Introduction:

In Parts I – III provided the disproof of BET (Brunauer-Emmitt-Teller<sup>1</sup>) equation and other “Henry’s law” and the Dubinin class of isotherms. They also provided statistical evidence that the QM derived equations were superior in precision and accuracy to the previous hypotheses. The accuracy argument is based on the use of the adsorbate molecule’s cross-sectional area as being an integral part of the QM perturbation derivation. In Part IV the QM derivation is provided.

In this part, Part V, the schicht equations are used to calculate microporosity. In Part VI the **D** function is used to calculate mesoporosity.

Part VII will continue with heat of adsorption and binary adsorption. How to calculate the heat of adsorption is well understood despite the dearth of excellent experimental evidence. Binary adsorption at this point is speculation. Some suggestions are put forward with weak evidence, but with perhaps some utility. In the future the QM base needs to be expanded for these areas.

## The “schichten” equations:

What is a “schicht?” In classical derivation, such as the BET, they talk about “layers.” To avoid the misunderstanding the analogue to “layers” is “schichten” (singular - “schicht”).

The word “layer” is reserved for the classical definitions. According to Brunauer <sup>2(p151)</sup> the “layer” concept used in other isotherm descriptions requires the 1<sup>st</sup> “layer” is to be complete before the 2<sup>nd</sup> “layer,” the 2<sup>nd</sup> before the 3<sup>rd</sup>, etc. Thus, a molecule in the 2<sup>nd</sup> “layer” is shielded from the surface forces by a molecule directly below it. His main argument was that the admolecules cannot transmit enough of the forces to have an affect succeeding “layers.” Of course, this was Brunauer’s assumption about other hypotheses and he did not apply this to his hypothesis.

This arrangement justified the shape seen for most isotherms but violates chemical thermodynamics. Brunauer used amount in a layer as a concentration. If he had used the areal density instead, that might lead to a better outcome, but he would also have granted that the other hypotheses. However, all the admolecules should be in equilibrium with the gas phase unless they were somehow chemically bonded and not a physically mobile adsorbate. Kinetics obviously can depend upon amount, but in the reverse reaction it would also, assuming the path of reaction is reversible to qualify as at equilibrium.

In contrast, the QM picture, one principle is that identical molecules are indistinguishable. Thus, one cannot distinguish a first schicht molecule from a molecule in a different schicht in a nonlocalized arrangement. A molecule belonging to the first schicht is treated the same as any other molecule regardless of its schicht. (One could also think of it as every molecule spends the same amount of time in each schicht on an average.)

The word “schicht” as used here (a familiar word for geologists) indicates a position where the residing molecules are and is not dependent upon molecules of a lower schicht for its chemical potential. The only chemical potential reference is against the liquid vapor (at the temperature of the adsorbent) and is the group potential of the adsorbate ensemble.

Never-the-less, if a schicht is blocked sterically, that schicht cannot be occupied. Any portion of the schicht that is not blocked is occupied according to the QM with the same areal density as the non-sterically block areas or open surface.

The schicht Aufbau is clear from an important observation to be made from the QM and GCPF equations. Notice that the greater the coverage or areal density, the lower is the available non-covered surface by the exponential function. Looking at it another way, how is the “open surface” being depleted. The GCPF indicates:

$$\theta_{MT} = \mathbf{exp}(-\theta) = \mathbf{exp}(-\Delta\chi) \quad \text{Equation 1}$$

Where  $\theta_{MT}$  is the “remaining” surface that can be filled. Perhaps  $\theta < 1$  indicate patches of zero areal density<sup>\*(p62)</sup> or a uniform depleted areal density that is a relative density less than 1. A mixture of both possibilities might be possible. The  $\Delta\chi$  is a function of pressure. At any rate, it has a lower average areal density. If that is the case than the first “layer” areal density,  $\theta_1$ , is given by:

$$\theta_1 = 1 - \mathbf{exp}(-\Delta\chi) \quad \text{Equation 2}$$

Subsequent “layers” can be calculated by assuming the first "layer" areal density is constant for any  $\Delta\chi$  and acts as part of the surface, which is implied by the original assumptions, then the following equation is obtained for the 2<sup>nd</sup> layer:

$$\theta_2 = 1 - \mathbf{exp}(-\Delta\chi + \theta_1) \quad \text{Equation 3}$$

This can be repeated over and over so:

$$\theta_n = 1 - \mathbf{exp}\left(-\Delta\chi + \sum_{m=1}^n \theta_m\right) \quad \text{Equation 4}$$

Of course, for the simple case if there is an infinite number of fillable schichten but can also be proved for  $m$  being finite:

$$\theta = \sum_{n=1}^{\infty} \theta_n = \sum_{n=1}^{\infty} \left\{ 1 - \mathbf{exp}\left(-\Delta\chi + \sum_{m=1}^n \theta_m\right) \right\} \quad \text{Equation 5}$$

An important point is to recognize that  $\theta$  may not equal  $n_a/n_m$ . For the ideal simple, sterically-nonrestricted adsorbent they are equal, even if there is heterogeneity. If there is steric limitations the distinction is important.  $\theta$  is the areal density of the adsorbates at positions where there is no total steric restrictions; whereas  $n_a/n_m$  is the amount adsorbed. Thus, for example, if there is room on the adsorbent for 1½ monolayers then the areal density of  $\theta_1$  is given by *Equation 3* and the areal density of  $\theta_2$  is given by *Equation 4* with  $n = 2$ . Using cardinal numbering for the amounts as well, on the other hand  $n_{a,1}/n_m$  is given also by *Equation 3* but  $n_{a,2}/n_m$  is ½ of *Equation 4* with  $n = 2$  as long as the steric hindrance allows it. This leads to a Lemma:

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\* QM does not specify which it is. Good question. Does it even matter? Brunauer believed it did and used the condensate patches as one of the “proofs” that the phase change started at the end of the isotherm. See Appendix IV for his comments.

*Lemma 1- For physisorption always the first schicht will always fill by Equation 2 so that  $n_a \Rightarrow n_m$  as  $P \Rightarrow P_{vap}$ :*

The first schicht will always fill to completion or:

$$n_{a,1} = n_m \theta_1 \quad \text{Equation 6}$$

A special law was mentioned previously called the log-law. This is obtained by rearranging Equation 3 to yield:

$$\frac{n_{a,1}}{n_m} = 1 + \frac{RT}{E_a} \ln \left( \frac{P}{P_{vap}} \right) \quad \text{Equation 7}$$

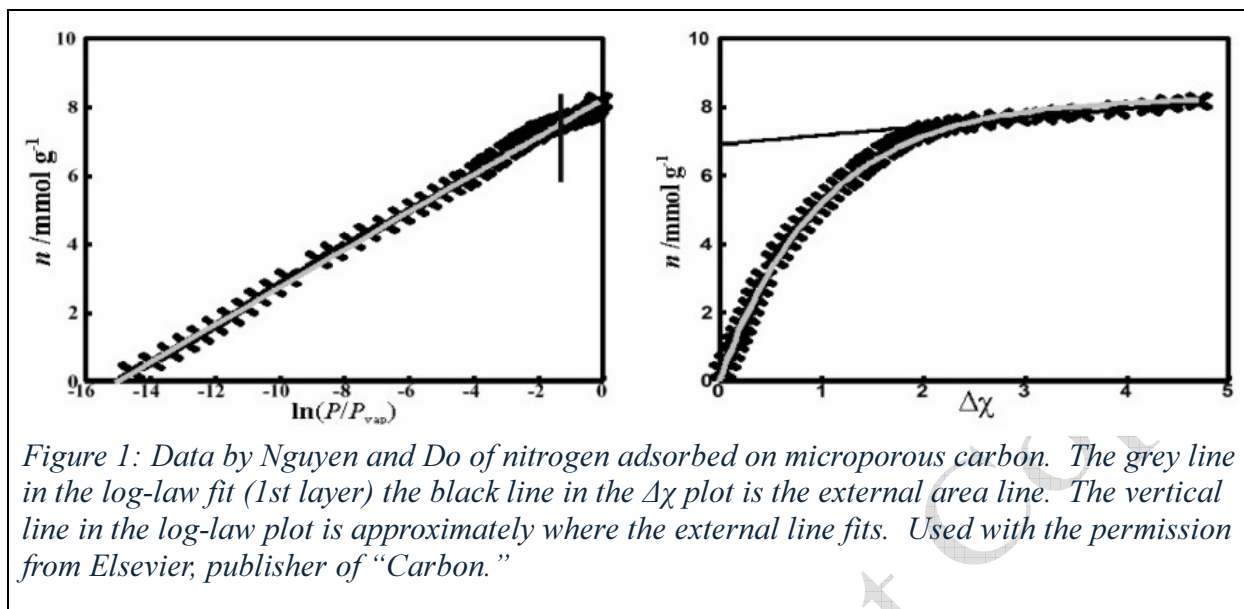
First schicht filling or microporosity seems to be often accompanied with other features. Some examples of this is provided. This lemma is obvious from Equation 6 and Equation 7. If it were not true, there would be no pore large enough to accommodate the adsorptive molecule.

### **Experimental Results involving 1<sup>st</sup> schicht involvement**

*Example 1 by Nguyen and Do again*

For data that one uses Equation 7 to analyze, often there are other features that need to be separated. This is illustrated by the next two examples illustrates 1) an external area and 2) a distinct heterogenous addition. The heterogenous addition uses the **Z** distribution as previously provided in Part II (see Appendix III). The external area is a simple linear fit to the  $\chi$ -plot at high pressures.

If one were to plot the amount adsorbed versus  $\ln(X)$  and obtain a straight line, this is an indicated that pores that can accommodate the adsorptive to only a monolayer, thus are microporous by the QM definition. Such was the case for the isotherm by Nguyen and Du<sup>3</sup> for external area. However, there is another feature present, that is, the area of the adsorbent that is not inside the pores. This was provided in Part I and again here as Figure 1. The full analysis of the was also presented in Part I and should now make more sense in Table 1:



Physical quantity	value	absolute precision	units	relative precision	Interpretation
$n_m =$	8.251	$\pm 0.020$	mmol g <sup>-1</sup>	0.24% FDR	monolayer equivalence
$\chi_\xi^* =$	-2.7118	$\pm 0.0027$			Threshold X transformed
$n_{\text{pore}} =$	6.91	$\pm 0.028$	mmol g <sup>-1</sup>	0.34% FDR	Amount that fill the pores
$n_{m, \text{ext}} =$	0.263	$\pm 0.007$	mmol g <sup>-1</sup>	0.094%FDR	Amount outside pores
$E_a^* =$	-9.763	$\pm 0.026$	kJ mol <sup>-1</sup>		Starting adsorption energy
$P_c/P_{\text{vap}}^* =$	$2.89 \times 10^{-7}$	$\pm 0.12 \times 10^{-7}$			Threshold relative pressure

\*The precision in these quantities is not as important since they are the independent variable.

A question is becoming more obvious and needed here is, "How does one compare fits?" "What criteria should be used?" Obvious, the fit to amount adsorbed should be a reference, but from sample to sample, the units and sample size might change. Thus, a relative comparison is used herein, that is, standard deviation of the amount adsorbed divided by the highest adsorbate amount used. This is given the acronym FDR for "of Full Data Range." Although, not precise, it is better than a nonparametric analysis such as the ranking systems some authors use that appear to not consider the magnitude of the data range. Again, one should not use any statistical test blindly and leave reasoning behind.

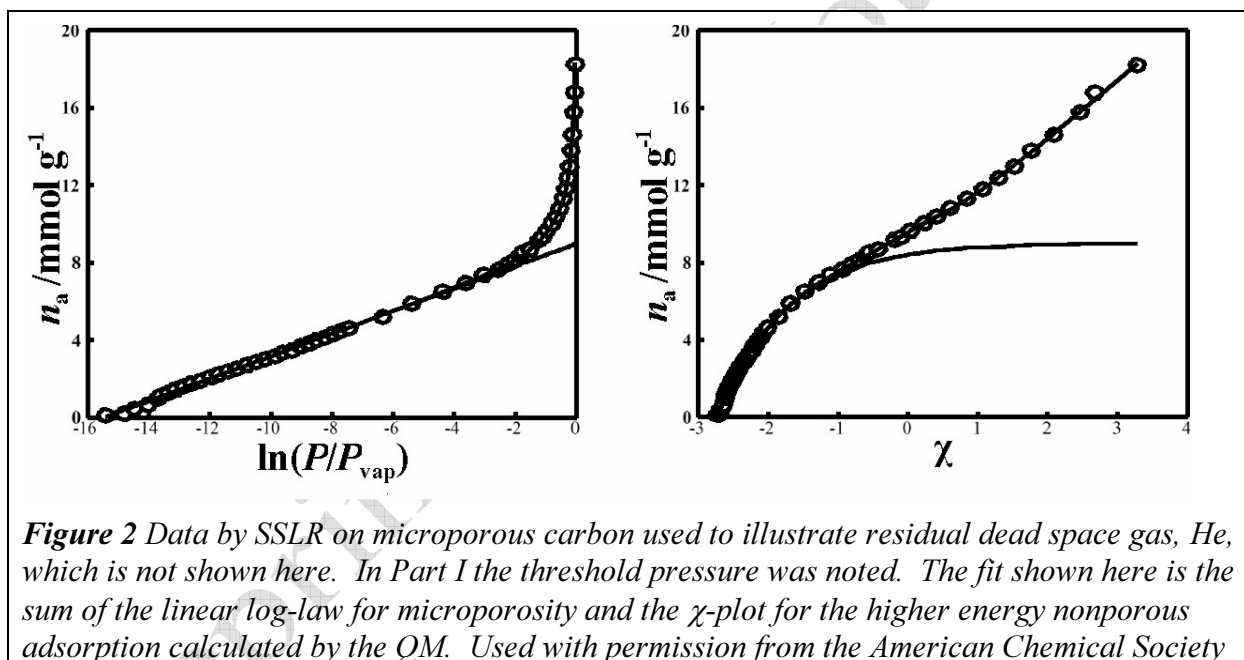
However, in this case the 0.24 %, 0.34% and 0.094 % FDR for all three  $n$  parameters is very acceptable. The use of this test is the standard deviation of  $n_a$  only and not in the independent variable or a combination of the two. By a normally self-imposed criteria of  $\leq 1$  FDR these are

quite acceptable\*. Thus, theoretically, a transform (usually for the abscissa) is for the independent variable only and has no effect on the value. The power of this test is that the comparison is against the data itself. However, it requires very good data, which is often hard to find.

*Example 2: Again, Silvestre-Alberto, Silvestre-Alberto, Llewellyn and Rodríguez-Reinoso data.*

The data by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso<sup>4</sup> (SSLR), used in Part I to demonstrate the log-law and the threshold pressure. The fits are in *Figure 2*

The early linear portion (log-law) of this plot indicate the microporosity was present, but there exists a deviation at higher pressures. This plot looks like the IUPAC round-robin investigations on Sterling FT and Vulcan G carbons<sup>5†</sup>, which could not be correctly analyzed due to lack of the low-pressure range. (Someone should repeat the adsorption on these systems using equipment that goes into the UHV. That might explain the frustrating results that were obtained previously.)



With a combination of the log-law and the  $\chi$ -plot, this data is relatively easy to analyze. In the early part of the isotherm the log-law, indicating a monolayer limit, dominates. With higher pressure, that seems to drift off to indicate an external area, but the normal  $\chi$ -plot, with heterogeneity, is indicated. (The log-law and  $\chi$ -plot must be added before the least squares routine is started.)

\* This is arbitrary, it come from the experience that a graph is displayed with data filling the space, one can see a 1% error without a magnifying glass. If there are other analyses then one could compare the statistics with a statical test like the F-test, but, this is tricky. One should not rely on close statistical test only but use some scientific reasoning

† Incorrectly analyzed in the textbook for this reason.



When analyzed with a least square fit with these two components included, a very good fit resulted. This should not be surprising for a charcoal adsorbent\*. In *Table 2* is the full analysis of this isotherm.

<i>Table 2 Data for N<sub>2</sub> adsorption on microporous C by SSRL</i>			
<i>quantity physical</i>	<i>value</i>	<i>Units</i>	<i>Description/meaning</i>
$n_1 =$	0.581	mmol g <sup>-1</sup>	Slope of the 1 <sup>st</sup> schicht line (homogeneous fit)
$\ln(P_c/P_{vap}) =$	-15.445		energy term relative to reference state
$E_a^\dagger =$	-10.02	kJ mol <sup>-1</sup>	differential energy at the start, (Threshold energy)
$\chi_s^\dagger =$	2.7379		threshold $\chi$
$n_{m,1}^* =$	8.99	mmol g <sup>-1</sup>	ordinate intercept for the 1 <sup>st</sup> schicht
$n_{ext,m} =$	2.967	mmol g <sup>-1</sup>	monolayer equ. of a monolayer for “1 <sup>st</sup> layer” schicht
$\chi_{s,p} =$	-0.6493		position of the pore distribution peak in the $\chi$ -plot
$\Delta\chi_p =$	0.770		position of the pore distribution peak in the $\Delta\chi$ -plot
$\langle E_p \rangle =$	4.1	J mol <sup>-1</sup>	Average energy of the pore – peak value
$s_p =$	0.649	J mol <sup>-1</sup>	The “spread” parameter of the <b>Z</b> function, 1 $\sigma$ .
$\Delta T =$	1.0254		Pressure correction due to higher than recorded $T$
$\sigma$ (fit) =	0.0856	mmol g <sup>-1</sup>	The standard deviation for the entire isotherm, 1 $\sigma$ .
$\sigma$ (% FDR) =	0.47 %		total for all $n_s$
* = $-m_1 \times \ln(P_c/P_{vap})$		† = derived quantities from isotherm parameters	

### *Example 3 Pore filling slightly past the monolayer filling*

There is no reason that there is exactly two types of pores, monolayer pore, called micropores here, or mesopores<sup>†</sup>. What would it be like to have a monolayer and a fraction of another layer? This may be where the investigator needs to remember not to go brain-dead. “What should this be called?”

An example of this is calculate here with micropores that contains at saturation a 1<sup>st</sup> layer plus some room for the 2<sup>nd</sup> “layer,” plus a small amount of external surface. This is from original data by: Madani, Kwong, Rodríguez-Reinoso, Biggs, Pendleton<sup>6</sup>, (MKR-RBP) and was kindly provided by Professors Madani and Pendleton. The adsorbent for this study was microporous

\* Activated carbon LMA 233 from olive stones heated in CO<sub>2</sub>. Manufactured by Advanced Materials. No other information is made available.

† If mesopores are present, the  $\chi$ -plot has a positive curvature past  $\chi \approx 0$  followed by a negative curvature.

carbon (poly-furfuryl alcohol based activate carbon) and the adsorptive-adsorbate was argon. This is shown in *Figure 3*.

In *Figure 3* the dashed line is the 1<sup>st</sup> schicht filling according to Lemma 1. The question could be, “How did you know that this was the proper line?” Of course, the fit was finally made using a least squares routine, but there was an advantage with having a partial amount of 2<sup>nd</sup> “layer.” That advantage was there was enough 2<sup>nd</sup> schicht to allow a straight line to fit the initial area of the  $\chi$ -plot. This is an alternative way to obtain  $n_{m,1}$ . To see how linear the plot becomes in low  $P$ , an enlargement of the start of the  $\Delta\chi$ -plot is shown in *Figure 4*.

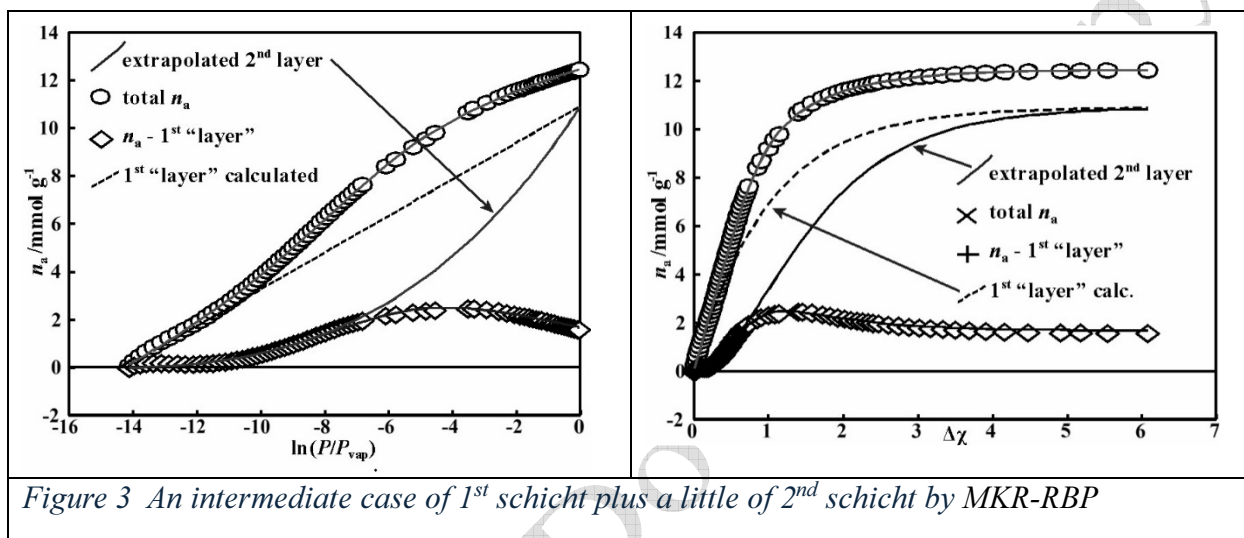
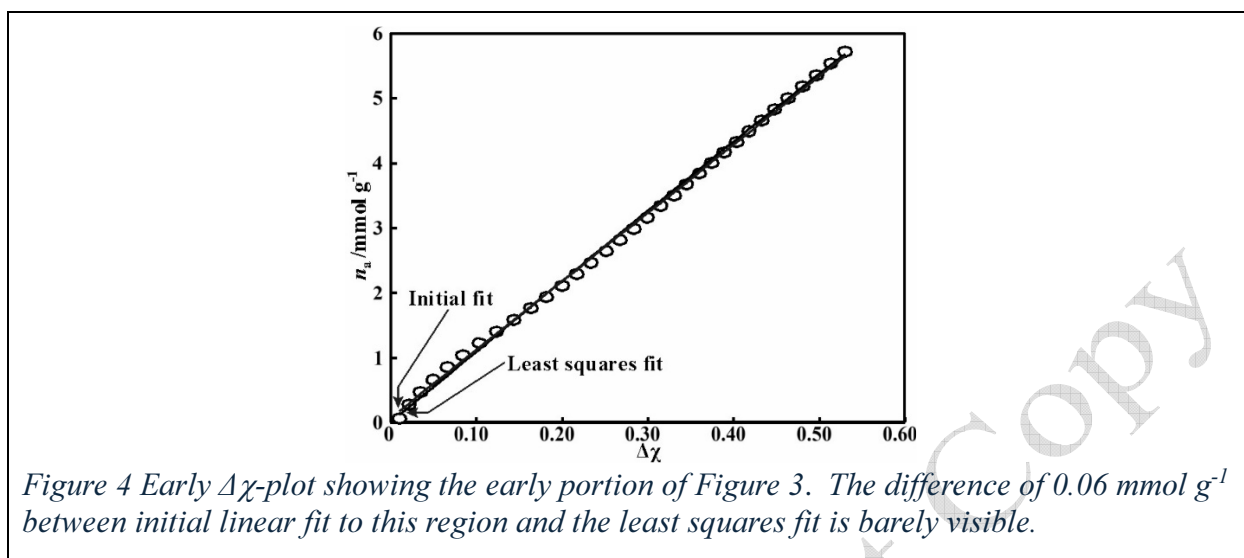


Figure 3 An intermediate case of 1<sup>st</sup> schicht plus a little of 2<sup>nd</sup> schicht by MKR-RBP

Data from (MKR-RBP) are used here to illustrate the method in *Figure 3*. Very little heterogeneity was detected, so it is a 4-parameter fit. Both the  $\chi$ -plot and the log-law plot are useful for this situation. However, the final least squares fit is the 4-parameter fit. The parameters are in *Table 3*.

$\chi_s^\dagger =$	-2.6591		$\ln(P_p/P_{\text{vap}})^* =$	-4.596	
$\therefore \ln(P_c/P_{\text{vap}})^* =$	-14.282		$\langle \chi_p \rangle^\dagger =$	-1.525	
$\therefore E_a^* =$	-10.37	$\text{kJ mol}^{-1}$	$\therefore \langle E_{\text{peak}} \rangle^* =$	-3.31	$\text{kJ mol}^{-1}$
$n_m^\dagger =$	10.84	$\text{mmol g}^{-1}$	$s^\ddagger =$	2.5410	$\text{in } \ln(P/P_{\text{vap}})$
$\sigma =$	0.059	$\text{mmol g}^{-1}$	$\sigma = (\% \text{FDR})$	0.47 %	

† indicates quantity derived from the original parameters ‡ The spread of the normal distribution . \* calculated from  $\chi$  values.



#### Lemma 1 and cannibalization:

Lemma 1 forces the filling on a straight line from  $n_a = 0$  to  $n_a = n_{m,1}$ . In doing so, some of the 2<sup>nd</sup> schicht may have to lose some of its density, such is the case here and a peak develops for this schicht at  $\ln(X) = -4.596$  with a spread = 2.5410. This is due to the development of addition steric interference in “stacking.” The decrease in the areal density in one schicht to fulfill the requirement of another schicht filling has been given the name “cannibalization.”

#### Conclusion for the QM and micropores:

In this Part IV the quantum mechanics (QM) was applied on the model of a “particle in the box with a tooth.” The “particle-in-the-box” is one of the simplest QM calculations that even first year chemistry undergraduates are familiar with. This is modified by placing a perturbation in the box, also an undergraduate undertaking. Then more and more identical particles are placed in the box and recalculated and renormalized after each perturbation. Using this single concept, and assuming a nonporous, homogeneous surface, the  $\chi$ -plot and  $\Delta\chi$ -plot are derived for the overall physisorption and Equation 2 through Equation 4 for the individual schichten filling. If only a monolayer is present then Equation 7, which is the rearranged Equation 2, is more convenient. Equation 7 is referred to as the log-law and the presence of monolayer adsorption is easier to recognize using it. Once derived, the equations are straight-forward, and no knowledge of QM is required.

However, the monolayer-only plot may not be the only feature seen in the log-law plot. There may be considerable external area or possibly additional 2<sup>nd</sup> or 3<sup>rd</sup> schicht filling adsorption or perhaps mesoporosity. By the 3<sup>rd</sup> schichten filling to a standard plot calculation would work well and either mesoporosity might be present or the anti-Gurvitsch rule could determine the porosity, as is done with classical standard curve determinations with, of course, a good estimate of the total surface monolayer equivalence.

So far from the equation derived in this section, one should be able to calculate homogeneous nonporous, or microporous adsorbents. One can distinguish between these two cases by whether an isotherm follows the  $\chi$ -plot, for non-porous homogeneous, or the log-law, for homogeneous microporous. The features of heterogeneity and the temperature was provided in Part III, which was necessary to demonstrate the real case being fit with the KJO data.

The property that the log-law is used for a fit is the QM definition of microporous in place of the IUPAC definition. However, as illustrated here, many isotherms have a combination of features, so an investigator needs to be able to recognize features when they are encountered.

The next questions are:

How does one determine if there is mesoporosity and how much? What is the pore size and at what energy? Micropore distribution is obvious, but what about mesopore, which is multilayer, pore distribution?

How can this be applied to multiple adsorbates?

Where is the promised ESW? This latter one is addressed here - coming up next in this paper.

In Part VI the phenomenon of mesoporosity will be addressed. First, the question of how to fit mesoporosity to yield parameters that one can use, and then what the interpretation is of the hysteresis, which is often seen with mesoporosity. The accompanying hysteresis is seldom below  $\chi = 0$ , for which the energy of adsorption is less than  $-648 \text{ J mol}^{-1}$ . A normal mesoporosity starts about  $-3 \text{ J mol}^{-1}$ , quite small in comparison to  $E_{as}$ , which often for ceramic material is below  $-5000 \text{ J mol}^{-1}$ . A shift in  $E_a$  of  $3 \text{ J mol}^{-1}$  is not normally directly observed and a shift of the entire isotherm to a slightly more negative value is not observable unless the isotherm has a near vertical section. Thus, there are cases of mesoporosity which disappears when the isotherm in the  $\chi$ -plot is shifted with a slight energy difference. This phenomenon has been observed, but it does not seem to be the sole origin of hysteresis.

### Disjoining Pressure and Excess Surface Work (ESW)

The main difference between  $\chi$  and ESW hypotheses is that  $\chi$  utilizes energy balance, whereas ESW utilizes the force balance.

Thus, another way of approaching the isotherm results and an explanation for and calculation of mesoporosity is the Excess Surface Work hypothesis. This hypothesis uses the concept of the disjoining pressure. Disjoining pressure was discovered and characterized by Derjaguin and Kusakov<sup>7</sup>, and Derjaguin, et al. starting in 1936( see a compendium<sup>8</sup>.) For many years, it had problems being recognized as correct but is now recognized by IUPAC. However, at the time of the BET formulation, it was mostly unknown or not widely accepted. Thus, neither QM nor disjoining pressure made it into the literature for physical adsorption until the 1980s, even though the resultant multilayer was known and often reviewed.

The equation for disjoining pressure is\*:

$$\Pi_d = \frac{1}{A} \left( \frac{\partial \mathbf{G}}{\partial z} \right) \Big|_{T,V,A} \quad \text{Equation 8}$$

---

\* Notice that in 3D this becomes a force tensor, a stumbling block in the 1920s

Where  $\Pi_d$  is the disjoining press,  $z$  is the distance from the surface,  $A$ , and  $\mathbf{G}$  is the Gibbs' energy. The equation for the ESW, excess surface work,  $\Phi$ , is defined as\*:

$$\Phi = n_a \bar{V} \Pi_d (n_a) \quad \text{Equation 9}$$

where  $\bar{V}$  is the molar volume<sup>†</sup>. Thus:

$$\Phi = -n_a \Delta_l^a \mu \quad \text{Equation 10}$$

Where  $\Phi$  is the Surface Excess Work, Since  $\Delta_l^a \mu$  is exothermic,  $\Phi$  is endothermic.<sup>‡</sup>  $\Pi_d$  has the following form as observed by B. V. Derjaguin and N. V. Churaev<sup>9</sup>, but also by M. Polanyi<sup>10,11,12,13,§,\*\*</sup> and with London,<sup>14</sup> deBoer and Zwikker,<sup>15,16,17,††</sup> and by E. L. Fuller, Jr.<sup>18,19,20,21,22,23,24,25,‡‡</sup> et al. who demonstrated it was an exponential decay for the energy function. These precedents are used to make the functional form for  $\Pi_d$  to have an exponential decay from the surface with a half decay,  $\lambda$ , which was later determined to be  $n_m$ :

$$\Pi_d = \Pi_0 \exp(-n_a / \lambda) \quad \text{Equation 11}$$

$$\Delta_l^a \mu = \mu_0 \exp(-n_a / \lambda) \quad \text{Equation 12}$$

where from Equation 9 and Equation 10, that  $H_0$  relates to  $\mu_0$  by:

$$\Delta_l^a \mu = -\bar{V} \Pi \Rightarrow \mu_0 = -\bar{V} \Pi_0 \quad \text{Equation 13}$$

It is a constant characteristic of the thermodynamic system. The association with the stated chemical potential change.  $\Phi$  is then given by:

$$\Phi = -n_a \bar{V} H_0 \exp(-n_a / \lambda) \quad \text{Equation 14}$$

For equilibrium, one differentiates negative  $\Phi$  and sets the answer to zero for a maximum. The  $\max(\Phi')$  is shown in *Figure 5* interpreted to be one monolayer equivalent. By relating the

\* This is the expansion of the adsorbate component,  $\Delta n_a \bar{V} = \Delta V$ , against the normal of the pressure tensor,  $\Pi_d$ . Thus, by the definitions provided here,  $\Pi_d > 0$ , going to the system, and  $\Delta_l^a \mu < 0$ , heat being transferred out.

† overbar or macron means molar the IUPAC alternate designation.

‡ Negating it is positive, that is, it takes work to remove the material from the surface.

§ Adamson referred to the Polarization Theory as “fundamentally correct. It accounts for the empirical fact that systems at the same value of  $RT \ln(P/P^0)$  [“o” means “<sub>vap</sub>”] are in essentially corresponding states.” He also stated, “There is thus little to choose between the various models, but partly because of tradition and familiarity and partly because  $v_m$  [here “m” for monolayer] enters in it so explicitly, the BET equation is in fact almost exclusively used.” This latter reason no longer applies due to QM.

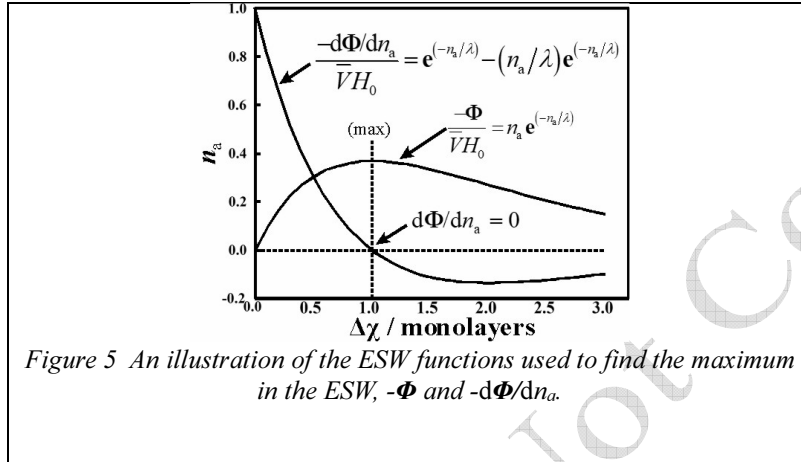
\*\* In his Science article Polanyi referred to BET as “orthodoxy.” He quotes Bertrand Russell about the danger of such authoritarianism. See Bertrand Russell's quote in section 18) **Final Conclusion**

†† deBoer and Zwikker had very little success of advancing the isotherm for two reasons, 1) they had a poor theoretical reason for their observation and 2) their adsorbent was at a higher temperature than the presumed temperature of their bath and an additional parameter was required; although they, like many others were not aware of how serious this temperature problem can be.

‡‡ Unfortunately, most of Fuller's huge cash of work is classified and will be unavailable until around 2070, if it isn't lost.

quantities to the QM through the chemical potential, this  $\mathbf{max}(-\Phi')$  is at  $\Delta\chi = 1$ . This confirms the monolayer assumption. The derivative is set to 0 to determine this maximum.

$$0 = -d\Phi(n_a)/dn_a = \bar{V}H_0 \left\{ \exp(-n_a/\lambda) - \frac{n_a}{\lambda} \exp(-n_a/\lambda) \right\} \quad \text{Equation 15}$$



The  $\Delta_l^a \mu$  is the change in the chemical potential transforming from the bulk liquid adsorptive to the adsorbate at the temperature of the adsorbent. Adolphs<sup>26272829</sup>, et al., related to the adsorptive/adsorbate to the chemical potential of Equation 13 which is related to the adsorptive pressure by:

$$\Delta_l^a \mu = -RT \ln(P/P_{\text{vap}}) \quad \text{Equation 16}$$

Eliminating the chemical potential between Equation 12 with Equation 16 yields the pressure dependence of the ESW formulation:

$$-RT \ln(P/P_{\text{vap}}) = \bar{V} \Pi_0 \exp(n_a/\lambda) \quad \text{Equation 17}$$

Rearranging slightly and taking the  $-\ln$  of both sides:

$$-\ln \left\{ -\ln \left( \frac{P}{P_{\text{vap}}} \right) \right\} = -\ln \left( \frac{\bar{V} \Pi_0}{RT} \right) + \frac{n_a}{\lambda} \quad \text{Equation 18}$$

This then is identical to the  $\chi$ -equation with:

$$\bar{E}_a = -\bar{V} \Pi_0 \quad \text{and} \quad \lambda = n_m \quad \text{Equation 19}$$

The ESW and QM are therefore equivalent. It turns out that the QM is more intuitive since the abscissa of the  $\Delta\chi$ -plot is a plot of monolayers equivalence and the  $\chi$ -plot abscissa is a plot of energy, as  $\ln(\bar{E}/RT)$ . Obviously, these plots are predicted by ESW as well. The ESW has another plot to yield the monolayer equivalence illustrated in Figure 5.

For micropores, the most convenient plot is the log-law. For mesoporosity it seems that the ESW plots are more straight-forward by modifying  $\Phi$  with the Kelvin equation or some other equation that seems appropriate. The QM approach adds a generalized distribution to the basic  $\chi$ -plot and the interpretation is not provided directly.

With the QM analysis, it is relatively easy to determine if there is microporosity and/or mesoporosity. It is probably best to do all three QM plots, the  $\chi$ -plot,  $\Delta\chi$ -plot and the log law. to get a full picture of what modifications are needed. Using the fitting equation available, one can typically obtain a fit to the data to within 1% FDR. One could use the fitted curve as smoothed data points for analysis with ESW. Such an interpretation will be provided in the mesopore section.

## Appendix I Symbol list

*English:*

$A$  = Dubinin pre-logarithm parameter –  $A \ln(X)^k$

$E_a$  = Preexponential parameter for the exponential free energy function

$E$  = System internal energy – normal units: J or kJ

$\mathbf{E}()$  = System internal energy function.

$k$  = Dubinin class of equation to  $A \ln(X)^k$

$n_a$  = amount adsorbate – normal units: mmol g<sup>-1</sup> usually but check what is being used.

$n_m$  = monolayer equivalence normal units same as  $n_a$

$n_{m, ext}$  = external monolayer equivalence normal units same as  $n_a$

$n_{pore}$  = amount of adsorbate in the mesopores units same as  $n_a$

$n_0$  = Dubinin Class: preexponential constant  $n_0$

$P$  = pressure of adsorptive – normal units: bar

$P_{vap}$  = The vapor pressure of the adsorptive at the temperature of the adsorbent.

$P_\zeta$  = The threshold pressure ( $\zeta$  = lower case termination sigma)

$X = P/P_{vap}$

$\bar{\quad}$  (overline or bar) = the symbol modification indicating “per mole.”\* Ex:  $\bar{E}$  molar energy

*Greek:*

$\Delta_l^a \bar{E}_T()$  = The change of the system internal energy going from the adsorptive liquid phase to the adsorbate phase at constant  $T$ . normal units J mol<sup>-1</sup> or kJ mol<sup>-1</sup>. Sometimes embellishments are left off.

$\Delta\chi(P_\zeta/P_{vap}) = \chi(P/P_{vap}) - \chi_\zeta(P_\zeta/P_{vap})$  – since the arguments are always  $P/P_{vap}$  and  $P_\zeta/P_{vap}$  they are allowed to be left off.

$\theta$  = the “coverage” for classical and “monolayer equivalence” for QM.

$\chi(P/P_{vap})$  = the function  $-\ln(-\ln(P/P_{vap}))$

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\* The IUPAC alternative convention for molar (enplethic) is used since there is a conflict with sub “m” meaning here “monolayer equivalence.

$\chi_{\zeta}(P_{\zeta}/P_{\text{vap}})$  = the function  $-\ln(-\ln(P_{\zeta}/P_{\text{vap}}))$

$\sigma$  = standard deviation of the dependent variable ( $\sigma_{\text{fit}}$  if there is a conflict.)

### Abbreviations:

QM = Quantum Mechanics

ESW = Excess Surface Work

FDR = of Full Data Range

BET = Brunauer, Emmitt and Teller

IUPAC = International Union of Pure and Applied Chemistry

### Appendix II – the Dubinin "thermodynamic criterion"

Polanyi<sup>10,11</sup> with London<sup>14</sup> proposed that a quantity  $A$  called the "Adsorption Potential," and Dubinin proposed using this as the starting point for porous sample analysis as a physical quantity for analysis for porous materials. This is given by *Equation 20*.

$$A := \mu_a - \mu_l = RT \ln \left( P_{\text{vap}} / P_a \right) \quad \text{Equation 20}$$

This leads to the Dubinin-Radushkevich<sup>30</sup> equation which Kaganer<sup>31,32</sup> applies to the non-porous surfaces to determine the relative surface area\*. The Kaganer's publications provides the rationale for the Dubinin "Thermodynamic criterion." The isotherms and some others in this classification fit the  $\chi$ -generated isotherms very well up to the inflection point at  $\chi = 0$ . At high values, they deviate yielding high values for monolayer equivalence. Such research confirm the relationship of Equation 21 for the dependence of  $A$  on temperature

$$\frac{\partial A}{\partial T} := \frac{\partial \Delta_l^a \mu}{\partial T} = 0 \quad \text{Equation 21}$$

This, of course, implies that the entropy of the transition from the liquid state to the adsorbed state is about zero. Indeed, the error using this assumption is experimentally and theoretically insignificant. This implies that the configuration of the bulk liquid and the adsorbate is very close to the same, or:

$$\therefore \Delta_l^a \mathbf{S} \approx 0 \Rightarrow \therefore \Delta_l^a \bar{\mathbf{E}} \approx RT \ln \left( P_{\text{vap}} / P \right) \quad \text{Equation 22}$$

See also Bering and Serpinski<sup>33</sup> and Bering, Dubinin and Serpinski<sup>34</sup> for further discussion of the thermodynamics and approximations leading to *Equation 22*. This equation forces the question, "Where is the transition to the liquid state." Brunauer's answer to this question that Fuller posed was that it was at  $P/P_{\text{vap}} = 1$ , consistent with Brunauer's writings<sup>35</sup>, and that it was not visible due to the experimental and other problems. However, if the transition is not near

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\* Similar in the "relative" sense to a standard curve method. Still requires a absolute measurement for which the BET was used.



$P_{\text{vap}}$ , then it must be when  $P$  approaches 0, otherwise, *Equation 22* predicts the energy goes to infinity as  $P \rightarrow 0$ .

Adamson<sup>36</sup> observed that the  $\ln(-\ln(P/P_{\text{vap}}))$  was the best empirical equation transform, but criticized it, quoting Brunauer<sup>37,\*</sup> on theoretical grounds<sup>†</sup> and the lack of  $v_m$  being explicit in the equation.

The eventual importance of *Equation 22* became apparent with Fuller's observation that the internal energy,  $\Delta_i^a E$  was exponential decay function of coverage. This observation had been noticed by others, including Brunauer, but the significance of this decay function was only obvious with the introduction of QM perturbation theory. The obviousness of this was apparent within seconds of Fuller mentioning this phenomenon to a novice physical chemist with a modest background in QM.

### Appendix III The Z distribution:

The distributions used are normally reserved for statistics based on the “normal distribution,” but in physics the distributions are usually based on the gaussian distribution. The only difference is a numerical constant. So why have I used distributions based upon the statistical formulas? Firstly, there is the question of what is being described, is it a law of physics or a random process, Secondly, the statistical functions present in most spread sheet programs. ... and thirdly, it doesn't matter so long as there is consistency. The functions that are available in my computer are presented in *Equations 23+*.

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\* I find it quite unusual for a publication that is either self-published or published only at one's institution to be taken as seriously as an open literature peer reviewed publication. The criticism does not appear to be available in any other place except the quote from his book and this is by an author which does not seem to have trouble publishing.

† Those grounds being it is impossible to transmit the force of the dipole induction through the first complete monolayer (that is, the classically dense layer by dense layer) sufficiently to get adsorption in the second and higher monolayers. Brunauer did not assume dense layers in his BET hypothesis, why is this disallowed for other hypotheses?

$$\mathbf{N}(x, \mu, s) = \frac{1}{\sqrt{2\pi s^2}} \exp\left(-\frac{1}{2}\left(\frac{x-\mu}{s}\right)^2\right)$$

$$\mathbf{D}(x, \mu, s) = \frac{1}{\sqrt{2\pi s^2}} \int_{-\infty}^{\tau=x} \exp\left(-\frac{1}{2}\left(\frac{\tau-\mu}{s}\right)^2\right) d\tau = \int_{-\infty}^{\tau=x} \mathbf{N}(x, \mu, s) d\tau =$$

$$\mathbf{Z}(x, \mu, s) = \int_{-\infty}^{\tau=x} \mathbf{D}(\tau, \mu, s) d\tau$$

$$\mathbf{Z}(x, \mu, s) = (x - \mu) \mathbf{D}(x, \mu, s) + \frac{2s^2}{\sqrt{\pi}} \mathbf{N}(x, \mu, s)$$

Equations 23+ The equations for function **N**, **D** and **Z** that are used throughout for publications by Condon.

A second distribution is theoretically called for. That is the inverse  $\chi$ . It describes the partial or full shutdown of the  $\chi$ -equation.

	$\exp\left\{-\exp\left(-\frac{x-\mu}{s}\right)\right\}$	Equation 24
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This distribution is very similar to the **Z** distribution with a little skewness.

#### Appendix IV Brunauer's comment about polarization etc<sup>2</sup>.

The following are comments that Brunauer state to discourage the isotherm descriptions that use the  $-\ln(-\ln(P/P_{\text{vap}}))$  transform.

In referred to forces of these transforms, "It is quite unlikely that a surface saturation with a complete layer of adsorbed molecules would be able to attract and adsorb a second layer of molecules."-page 62 and later page 143, "The reason is that the polarization of the second layer of adsorbed gas by the first layer is already much too small to constitute the major portion of the binding energy between the two adsorbed layers." Notice that he assumes that the first layer must be complete before the second layer can start to form, an assumption that he himself did not make in the derivation of the BET. (Actually, he assumed the *amount* in the layer affected the chemical potential, to yield some attractions in the higher layers. This seems to be an even worse assumption.)

This could also be the mistake of not recognizing what the reference pressure is in the isotherm. If one assumes that the reference pressure is the standard thermodynamic convention, one would, indeed end up with some weird results. That result would be below 1 bar, only the first layer would adsorb and above 1 bar the adsorption would run away.

In classical thinking, a layer is like a coat of paint. First one layer is deposited and when that is complete, then layer number 2 is deposited, etc. This is why the QM definition of "layer" is

placed in quotes to indicate that theoretically the layer is never complete, although for values near  $P/P_{\text{vap}}$ , an engineer would say, “good enough.”

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