

Title:

**Part IV: QM of Physisorption -
QM Equations χ -plot, $\Delta\chi$ -plot, Log-law and Schichten**

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Contents:

Title:	1
Part IV: QM of Physisorption -	1
QM Equations χ-plot, $\Delta\chi$-plot, Log-law and Schichten	1
Abstract:	3
Introduction:	5
<i>A Quick Review</i>	<i>5</i>
<i>The Content of this Part IV</i>	<i>5</i>
<i>In defense of Quantum Mechanics</i>	<i>6</i>
Quantum Mechanics: The Particle-in-the-Box-with-a-Tooth Calculation:	6
<i>a) Assumptions:</i>	<i>6</i>
<i>b) Adding a Positive Perturbation for the "Particle in the Box":</i>	<i>8</i>
<i>c) As other Admolecules Jump-In and the Origin of the Energy Exponential Decay.</i>	<i>10</i>
The Grand Canonical Partition Function (GCPF)	12
<i>Interpretation of χ and $\Delta\chi$ from the GCPF:</i>	<i>15</i>
The Schicht Equations:	17
Conclusion about the QM derivation	17
Disjoining Pressure and Excess Surface Work (ESW)	18
Conclusion about the QM derivation	20
Conclusion about the QM derivation	21
Conclusion Concerning ESW	21
Appendix I – the Dubinin "thermodynamic criterion"	22
Appendix II The "distributions":	23
Acknowledgements:	25
Funding:	25
Data and materials availability:	25
References:	25

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**Part IV: QM of Physisorption -
QM Equations χ -plot, $\Delta\chi$ -plot, Log-law and Schichten**

James B. Condon

Abstract:

The Quantum Mechanical derivation (QM) of the physisorption equations uses the Hellmann-Feynman¹ Theorem. These equations were reported earlier using two methods, perturbation theory² and the WKB³ approximation with, of course, the same results. The resultant equations can be readily used by someone not familiar with QM. However, an understanding of the origin is something the expert in physisorption should have. The QM followed by the Grand Canonical Partition Function (GCPF) yields the “simple” case, which is multilayered and uninhibited adsorption, with the Polanyi and London, with DeBoer and Zwikker, and with Fuller, et al., in **Error! Reference source not found.**:

$$n_a/n_m = \theta = \Delta\chi U(\Delta\chi) \quad \Delta\chi = \chi - \chi_\zeta$$

where $\chi = -\ln\{-\ln(P/P_{\text{vap}})\}$ and $\chi_\zeta = -\ln\{-\ln(P_\zeta/P_{\text{vap}})\}$

Equation 1

Where n_a in the “simple” case here is the amount adsorbed, n_m , is the monolayer equivalence. Thus θ is the projection of the total areal density. P_ζ is the threshold pressure. $P_\zeta = \exp(-\bar{E}_a/RT)$ yielding the preexponential for the system internal energy function given in **Error! Reference source not found.**:

$$\Delta_\gamma^a \mathbf{E}(-\chi) = E_a \mathbf{exp}(-\Delta\chi) \equiv E_a \mathbf{exp}(-n_a/n_m)$$

Equation 2

The QM also yields the following equations for the individual schicht* (or “layer”) areal densities:

$$\theta_1 = 1 - \mathbf{exp}(-\Delta\chi)$$

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

⋮

$$\theta_{n+1} = 1 - \mathbf{exp}\left(-\Delta\chi + \sum_{m=1}^n \theta_m\right)$$

$$\Rightarrow \theta = \sum_{m=1}^{\infty} \theta_m \equiv \Delta\chi \geq 0$$

Equation 3

* The word “layers” has too much association with the classical meaning of a dense layer, so the word “schicht” is being used when individual positions in the stacking is being addressed and not the dense layers. Thus, the words “monolayer” and “monolayer equivalence” are retained with the meaning of amount as defined.

The first equation may be rearranged to *Equation 4*, the log-law, for steric restriction to a single monolayer:

$$n_{a,1} = n_m + \frac{n_m RT}{\bar{E}_a} \ln \left(\frac{P}{P_{\text{vap}}} \right)$$

Equation 4

These equations confirms the Dubinin “Thermodynamic criterion” where $\Delta^a S \approx 0$.

In the final section, the ESW hypothesis is presented, which is another way to start these equations.

Introduction:

A Quick Review

In Parts I – III the disproof of a class of equation for physisorption was provided along with examples of how poorly, both in accuracy and precision the BET (Brunauer-Emmitt-Teller⁴) equation. This class of isotherms are referred to as “Henry’s law” hypotheses since they predict that the isotherm extrapolates to $[X, n_a] = [0,0]$, where $X = P/P_{\text{vap}}$. By not extrapolating to $[0,0]$ a critical property of the BET fails. thus rendering it invalid. It was also demonstrated that the various isotherm description by the Dubinin group failed the same test as well.

For accuracy and precision, a comparison hypothesis to the BET was the QM/ESW (Quantum Mechanical/Excess Surface Work) hypothesis. By any possible statistical test, the BET yielded much poor results, even when only 2/3rds of the total results for the BET is ignored, as is commonly done. However, the comparison used all the data for QM/ESW.

In the previous parts, Part I through Part III, the derived equations were assumed. This might seem to be a novel approach. However, it seemed necessary to be convincing enough to end the classical thinking involving sites, chemical equilibrium, etc. This provides the believable possibility to concentrate on the intermolecular forces instead. It also seemed necessary to define carefully what the various word meanings are, for without the clear understanding of such terms as “system,” “physisorption,” etc., this series is open to unjustified criticism, as 40 years of experience indicates.

The Content of this Part IV

This part, Part IV, starts with a potential energy box with infinitely high boundaries and the bottom of the box being zero for the reference energy:

- 1) The assumptions going into the quantum mechanical derivation of the “big box” with a tooth^{*}, the 1st admolecule that enters the box yield the usual “particle in the box” but also becomes are perturbation for the 2nd particle.

* The “tooth” does not need to be a squared area times a constant energy as used in this derivation. Indeed, what is needed is to identify the volume of the potential energy times the area it is spread over. It could be any energy-areal volume perturbation, e.g. a wave and is determined by an integral of the wave possibilities times the variable energy.

- 2) The QM solution is “a particle in the box with a tooth” for the 2nd admolecule.
- 3) The 1st and 2nd particles are now new non-local energy perturbations, able to randomly overlap, for the 3rd molecule.
- 4) This continues for the 4th, the 5th,...the Nth particle that enters the box with new reference energies.
- 5) The solution for the Grand Canonical Partition Function yielding the normal SIO standard state as the reference state.
- 6) Demonstration of the relationship to a new reference state, which is the liquid state at the temperature of the adsorbent.
- 7) The reasoning for the schichten equations
- 8) Example calculations and expansion to use with some more features.
 - a. Adding in external “area.”
 - b. Adding in using heterogeneity for “external area” and monolayer converge
 - c. Calculation of a monolayer plus a fractional schicht and cannibalization.
- 9) A start of the ESW derivation and how it is related to the QM

In defense of Quantum Mechanics

The most common objective presented by most chemists, engineers, and some physicist is that the adsorbate molecules are “too big and massive” to behave according to quantum mechanics. The argument against QM is that molecules are too big to behave like a wave. This is, of course, bogus. This argument is widely disputed by physics literature. Firstly, why would QM for high mass molecules not apply? Physics dictates, today, that all matter is controlled by QM. Secondly, this argument has been proven false by several Young’s experiments^{5,6}. These molecules include He atoms (α), I₂ molecules⁷ (254 amu), C₆₀ “buckyballs”^{8,9} (720 amu,) superposition with TPPS-20^{*,10}, and indeed, quantum interference has been observed with a series fluorinated thiol chains with masses above 10,000 amu¹¹. Furthermore, the use of viruses may soon be attempted¹². If this had not been true it would have disproved the linearity of QM, something at this time would be a big shock to physics. Thus, the wave nature of adsorbate molecules’ probability is expected and is made the first assumption of the derivation and the modern QM concepts are expected with superposition and delocalization. These are firm and well-based assumptions, despite tests that continues today!

Quantum Mechanics: The Particle-in-the-Box-with-a-Tooth Calculation:

a) Assumptions:

The quantum mechanical (QM) description is reasonable for any theoretical chemist and considered valid today. Not only that, but if the QM were not observed in physical adsorption,

* tetrakis(pentafluorophenyl)porphyrin

then some basic properties and modern QM would be disproved*. The following is the simple case for only one type of adsorptive being measured. (Going to binary mixtures gets a little more complicated although there are examples of simple binary cases.) The derivation first must consider the “simple case,” that is, the adsorbent is homogeneous, flat and non-porous surface. Expansion to the more complex cases will use the “simple case” and add to it “features” or modifications. These additions could be considered perturbations beyond the “simple case.” The underlying theory remains, and these features are inserted.

The critical assumption in the use of QM is a technique called separation of variables. The assumption for the model is that the wave function of an adsorbate particle may be separable into two geometrical parts. These are:

Part 1 is parallel to the plane of the surface (x, y)[†]. This is the most important part and generates the isotherm. It specifies the amount of adsorbate molecules directly in contact with the surface and the amount in subsequent schichten. Molecules are indistinguishable, which is an important concept in QM. Part 1 yields n_m , the monolayer equivalence from the isotherm directly without modeling or the use of standard plots. Furthermore, the heats of adsorption obtained from the equations are in excellent agreement with those obtained by calorimetry.

Part 2 is the wave function normal to the surface (z). From the schicht amounts, one obtains an estimate of the amount that fills the pores from each schicht. For actual vertical distance from the surface, one needs to assume an intermolecular potential, such as a Lennard-Jones potential to get the distributions between the schichten.

The difference between these assumptions and the normal QM treatment is that the xy -plane is treated differently from the z direction. Part 1 involves no arbitrary input parameters. Part 2, if pursued or needed, requires some geometric assumptions such as a Lennard-Jones potential or a hard-core radius for the admolecules. Part 1 yields answers of adsorption energy and monolayer equivalence for the simple case. Converting monolayer equivalence, n_m , to geometrical area is not as easy as the BET (the IUPAC standard) formulation naively assumes.

The calculation was originally based on non-localization, that is, the specifics to the potentials of individual atoms and molecules on the surface is not detected, but rather only the overall potential. This assumption is used for liquids, in contrast to solids, where the local potential becomes important. (This is reasonable since the temperature for the isotherms are usually between the T_c and T_{MP} .) This assumption has also become common in other physisorption calculations such as NLDFT, where NL stands for “Non-Local,” or QSDFT where QS stands for “Quenched Solid.” Thus, the energy is localized neither by the surface atoms nor the admolecules. Once a molecule is adsorbed, it becomes part of the system, as defined above.

For a nonporous homogeneous surface, if the resulting equations are fit to the isotherm, then there are two output parameters, n_m , and E_a . The fit for “simple” cases is a simple linear regression. (Adding features requires non-linear least squares routines.) If porosity exists, Part V is used to convert the extra output parameters to radii and volumes.

* The disproof would be by the most rigorous of theories disproofs, that is, showing that a phenomenon that is predicted is false.

† Here normal Cartesian coordinates are used. The use of other coordinates, such as cylindrical coordinates as augmentations might be an interesting approach.

b) *Adding a Positive Perturbation for the “Particle in the Box”**:

To start a potential box with infinite walls (in potential) and a particle is placed in this box. The various dimensions will allow certain approximations that are not strictly needed but makes the presentation easier. These dimensions are that the adsorbate molecule is extremely small compared to the adsorbent aliquot. (The surface aliquots are typically in the micro scale whereas the admolecules are on the nano scale. Thus, the squares of the yields a factor of $\sim 1 \times 10^6$, certainly big enough.) These approximations have been referred to as the “big-box approximation” in the original publications^{†,13,14}.

A generalized quick derivation using the Hellmann-Feynman^{1,15,16,17} theorem will demonstrate this. The answer to this without perturbation is very easy. Firstly, the QM calculation for the particle in the box yields for the lowest (ground) state a value given by the one-dimensional (1D) equation[‡]:

$$E(n=1) = \frac{\pi^2 \hbar^2}{2mL^2} \quad \text{Equation 5}$$

For argon the energy for a one micrometer in 1D is $\sim 0.5 \times 10^{-6}$ or in 2 dimensions (2D) is about $1 \times 10^{-6} \text{ J mol}^{-1}$. One needs to be on the nanometer range to be perhaps significant, since a 2D surface of 1 nm yields an energy of 1.0 J mol^{-1} . This is still small compared to a typical physisorption energies of about 3 to 30 kJ mol^{-1} . Thus, one can ignore the difference between the base energy and the ground state with little error. This is merely a simplification, if there is a need, this can be altered.

After the first molecule enters the box, with the energy given by *Equation 5* and the wave function is given by:

$$E|\Psi\rangle = \hat{\mathbf{H}}|\Psi\rangle \quad \text{Equation 6}$$

Now the box contains a perturbation which itself is a wave. The second particle enters the box, and it "sees" the first particle. (This was called a particle in the box with a “tooth,” rather than a hole.) This particle is also a wave, however, both particles are identical and indistinguishable, but the two standing waves are together stable in energy. Thus, it is not necessary to use time dependent wave vectors. The addition of the perturbation would be:

$$\{E + \delta E\}|\Psi\rangle = \{\hat{\mathbf{H}} + \delta \mathbf{H}\}|\Psi\rangle \quad \text{Equation 7}$$

where the δ s designate perturbation. Thus, multiplying both side by $\langle \Psi^* |$:

* A short-cut is taken using the Hellmann-Feynman theorem since only the energy change is needed. For a more complete derivation with the resultant wave functions see the 2nd edition of “Surface Area and Porosity Determination by physisorption. 2nd ed.” by J. B. Condon, Elsevier Press, Netherlands ISBN 978-0-12-818785-2.

† There is even a shorter path. Physicist would simply say that to the 1st order, the energy is a weighted energy-space average over a confined space. The energy-space is $a\beta$ and the confined space is A . Thus $a\beta/A$.

‡The Hellmann-Feynman theorem can be applied in any coordinate system, and it is not necessary to do the full QM to be rigorous. In the book a full QM treatment is presented so one could calculate the answer for the maximum uncertainty.

$$\langle \psi^* | \{E + \delta E\} | \psi \rangle = \langle \psi^* | \hat{\mathbf{H}} + \delta \mathbf{H} | \psi \rangle \quad \text{Equation 8}$$

E and δE are constants, so:

$$E + \delta E = \frac{\langle \psi^* | \hat{\mathbf{H}} + \delta \mathbf{H} | \psi \rangle}{\langle \psi^* | \psi \rangle} = \hat{\mathbf{H}} + \frac{\langle \psi^* | \delta \mathbf{H} | \psi \rangle}{\langle \psi^* | \psi \rangle} \quad \text{Equation 9}$$

(Renormalizing is usually not needed due to the smallness of the perturbation, however, the renormalization prevents a buildup of a systematic error.) The increments designated with δ are very small so one should be able to use assumptions* of the Hellmann-Feynman^{1,15,16,17} theorem[†]:

$$\frac{\partial E}{\partial \lambda} = \int \langle \psi | \frac{\partial \mathbf{H}}{\partial \lambda} | \psi \rangle d\psi \quad \text{Equation 10}$$

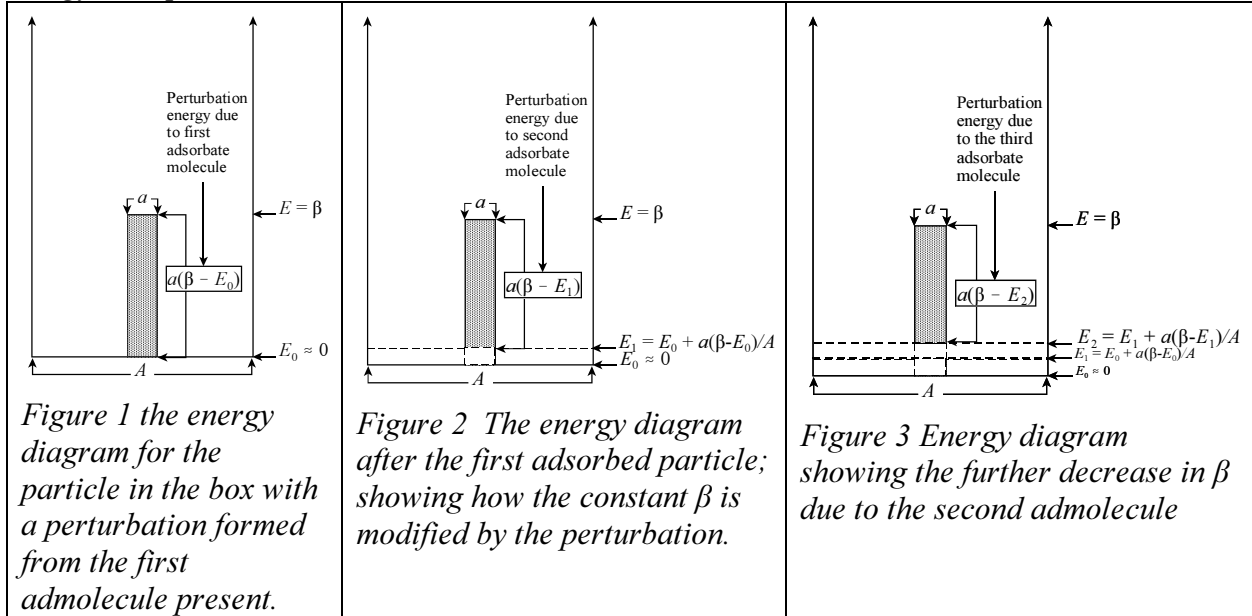
with the integral over all space. To continue, it is assumed that δH

1) is a function of space only and not time and

2) can be expressed as some weighted value to yield δH after integration.

$$\int_{\infty} \delta E d\lambda = \delta \mathbf{H} \int_{a < E} \langle \psi^* | \psi \rangle d\lambda \quad \therefore \quad \delta E = \delta \mathbf{H} \quad \text{Equation 11}$$

However, to be clear, the δE will vary as the adsorption continues as a function of $\mathbf{E}(\theta)$ and the energy of vaporization.



* That is $\langle \psi_\lambda^* | \psi_\lambda \rangle = 1$ and $d\langle \psi_\lambda^* | \psi_\lambda \rangle / d\lambda = 0$ where λ are the generalized spatial coordinates, for example x, y and z.

† This is the 7th equation in the Feynman article after equation (2). This is the easiest way. You can take the long way by referencing some QM textbook. For example, "Introduction to Quantum Mechanics by Chambers W. Sherwin, from Holt, Rinehart and Winston, New York." Thus, now I have presented three or four different ways of coming to the same answer.

At this point diagrams would be useful*. For the one dimension, a is the area of the perturbation (looking forward to 2 D) and A is the area of the 2D box. This is shown in Figure 1 for the perturbation after the first admolecule is on the surface. The ground state and the bottom of the box are approximately the same value (~ 0 .) The energy of the perturbation is β and the area of the box is A . The energy of β is referenced against E_0 . The perturbation changes as more admolecules are physisorbed thus changing the base energy E_0 to E_1, E_2, E_3, \dots

The perturbation, called a particle-in-box-with-a-tooth, to describe *Figure 1* through *Figure 3*, is then.

$$\delta \mathbf{H} = \frac{a\beta}{\langle \Psi^* | | \Psi \rangle} = \frac{a\beta}{\int_{-\infty}^{+\infty} (\mathbf{U}(\tau) - \mathbf{U}(\tau + A)) d\tau} \quad \text{Equation 12}$$

where “ $d\tau$ ” is the 2D. However, according to *Equation 12* the normalization is limited to the area A and outside this space it is zero since the height of the box walls are infinite. Thus, since δH is a function distance only and the integral over the area, A , is very close to the same as the integral over all space[†] then equation becomes:

$$\delta \mathbf{H} = \frac{a\beta}{A} \quad \text{Equation 13}$$

Thus, E_1 is given by:

$$E_1 := E_0 + \delta E = E_0 + \frac{a\beta}{A} \quad \text{Equation 14}$$

However, since $E_0 \approx 0$ as the reference then:

$$E_1 = x\beta \text{ where: } x = a/A \quad \text{Equation 15}$$

E_1 is the energy that the second admolecule will experience upon adsorption.

c) As other Admolecules Jump-In and the Origin of the Energy Exponential Decay.

In *Figure 1* the admolecule provides a perturbation for the third molecule of:

$$a(\beta - E_1)/A \quad \text{Equation 16}$$

$$\text{So: } E_2 = E_1 + a(\beta - E_1)/A = x\beta + x\beta - x^2\beta \quad \text{Equation 17}$$

$$\text{Competing the "square:" } E_2 = -\beta(1 - 2x + x^2) + \beta \equiv -\beta(1 - x)^2 + \beta \quad \text{Equation 18}$$

This begins the sequence based on the binomial lemma with $y_n = E_n/\beta$:

$$y_n = 1 - (1 - x)^n \quad \text{Equation 19}$$

$$y_{n+1} = 1 - (1 - x)^{n+1} + x(1 - x)^n \quad \text{Equation 20}$$

* Some notations have changed from previous notations. This is being done to avoid confusion with look-alike characters, for example Italic “a” and Greek “ α ”. Another reason the “threshold” symbol subscript “c” is replace with Greek “ ς ” since “c” is used by IUAC for the critical P_c and T_c .

[†] Outside the box, the function decay exponentially with an exponential decay constant that is high compared to the picoscale. Even the integral to 13×10^9 light years makes approximately no difference.

$$y_{n+1} = 1 - (1-x)^{n+1} \quad \text{Equation 21}$$

Back substituting and using traditional N in place of n :

$$E_N = -\beta \left\{ 1 - \left(1 - \frac{a}{A} \right)^N \right\} + \beta, N \geq 0 \quad \text{Equation 22}$$

The cross-section of a simple molecule is about 0.2 to 1 nm and the adsorbent surface aliquots are in the range of micrometers. Squaring these numbers and dividing one gets a factor of at least 1×10^6 . So, an approximation of an exponential function for the second term in the brackets may be made provided there is a relationship between n and x . This relationship is called the monolayer equivalence, or classically, the coverage (or for QM the normalized areal density:)

$$\theta = \frac{Na}{A} \quad \therefore N = \frac{A\theta}{a} \quad \text{Equation 23}$$

(Apologizes for the next step, which should be simple, but there has been in the past strong opposition to the approximation that follows. If

Equation 26 is obvious to you then skip to Equation 28.) The meaning of x is reset here:

Let:	$x = -\frac{A}{a} \quad \text{so : } N = x(-\theta)$	Equation 24
Then:	$\left(1 - \frac{a}{A} \right)^N \equiv \left\{ \left(1 + \frac{1}{x} \right)^x \right\}^{-\theta}$	Equation 25
But for large x by the definition of the e function:	$\lim_{x \rightarrow \infty} \left\{ \left(1 + \frac{1}{x} \right)^x \right\}^{-\theta} \approx \mathbf{exp}(-\theta)$	Equation 26
Equation 22 with Equation 26:	$E_N = \beta - \beta \mathbf{exp}(-\theta)$	Equation 27

The question is how big x needs to be. The following are calculations.

For a 1% error $x = 50$.

For 0.1% error this is $x = 500$.

For 0.01% error this is $x = 5000$.

Thus, the ratio of A to a is unlikely to present a significant error in this approximation. Perhaps for biological applications, such as channel gates, etc., it may matter.

The result for the QM derived energy for the N^{th} molecule is

$$\mathbf{E}(N) = \beta - \beta \mathbf{exp}(-\theta) \quad \text{Equation 28}$$

One would tend to think that the upper limit would be the saturating energy, in other words the $\Delta_i^3 \mathbf{E}(P_{\text{vap}}(T_a)) = \beta$. However, at this point β is an arbitrary constant. The proof of this comes with the Grand Canonical Partition Function. This should have been recognized with the derivation of the Dubinin “thermodynamic criterion” (See Appendix I.)

The Grand Canonical Partition Function (GCPF)

In the above equations, β is an arbitrary constant and the functional relationship to pressure is not obvious, but reasonable. The meaning for β and the pressure dependence will now be determined using the Grand Canonical Partition Function (GCPF). The system, the adsorbate and adsorbent, is an open system therefore the GCPT is an appropriate technique to determine thermodynamics.

First recall that the base energy for the calculations for β was the bottom of the well seen in *Figure 1*. The surrounding energy however is not defined by this energy but by the standard thermodynamic convention, designated with the symbol “ \ominus ,” as shown in *Figure 4*. This figure shows the shift in the reference energy to 1 bar for the adsorptive.

The energy is changed in an open system by changes due to the release of energy by the adsorption:

1. From the adsorbate surface interaction with adsorbate molecules
2. By adsorbate-adsorbate interaction and
3. The energy indicated by the change of state for the adsorptive

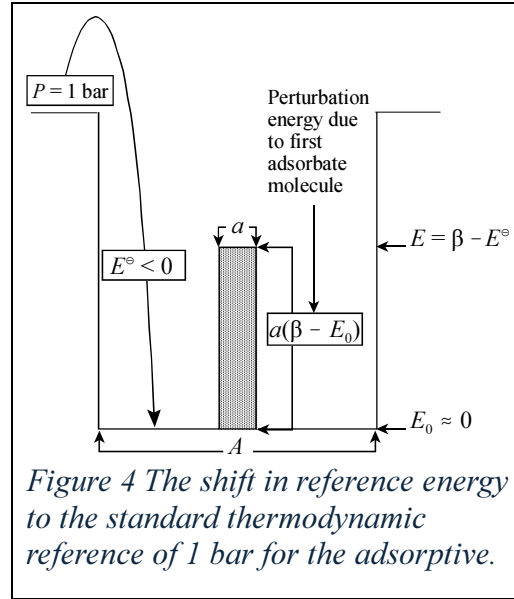
The first of these energies is what the particle-in-box-with-a-tooth provides. The second one must be the interaction between the adsorbed molecules, and it must be between all the molecules or:

$$N(E^{\ominus} - \beta) := N\varepsilon \quad \text{Equation 29}$$

Where here the quantity ε is defined as an independent quantity from the reference state. Thus, ε is now the unknown constant in place of β . The third quantity is given by the canonical partition function for the

adsorptive gas, in other words, what the gas loses the system obtains. So, these three quantities are the energies that go into the GCPF. At this point a conversion to a new reference state becomes convenient.

This new reference state is the liquid vapor pressure of the adsorbent at the temperature of the adsorbent. This is normally referred to as the “relative pressure.” This is illustrated in *Figure 4*.



The system internal energy reference state is then defined by the difference between the standard state and the relative pressure., which uses the symbol E_a .

$$E_a = (E^\ominus - \varepsilon) \quad \text{Equation 30}$$

Thus, the energy with the relative pressure as the reference pressure, the energy increase for the system from the internal energy of the vapor is for the N^{th} adsorbate molecule:

$$\Delta_i^a \mathbf{E}(N) = E_a \mathbf{exp}(N) + \varepsilon \quad \text{Equation 31}$$

So, summation for the N molecules is:

$$\sum_N \Delta_i^a \mathbf{E}(N) \cong E_a \int_0^N \mathbf{exp}(-\theta) dx + N\varepsilon \quad \text{Equation 32}$$

This can be used for the energy terms in the exponential term of the GCPF. Thus, the GCPF is given by:

$$\prod_{GCPF} = \sum_N (\lambda Z)^N \mathbf{exp} \left[- \left(E_a \int_0^N \mathbf{exp}(-\theta) dm - N\varepsilon + \frac{1}{2} N\theta_1 kT \right) / kT \right] \quad \text{Equation 33}$$

The first term is the canonical partition function of the adsorptive gas. The first term in the exponent is the energy from *Equation 33*. It is assumed that there are no changes in rotational or internal vibration for the adsorptive-adsorbate molecule change. This can obviously be changed with the determination that these are present and are modified by adsorption. There is a fourth

term added here of $\frac{1}{2}N\theta_1kT$, which accounts for the loss of one translational mode for molecules touching the surface. This quantity is very small compared to normal energies observed with physisorption, so it also is ignored here.

Thus, *the Dubinin thermodynamic criterion* recognizes that the internal vibrations, rotation modes and the $\frac{1}{2}N\theta_1kT$ are normally insignificant to the overall adsorption energy, therefore:

$$\Delta_l^a S \approx 0 \quad \text{Equation 34}$$

The usual method is to take the natural log of Ξ (which yields the grand canonical potential) and then differentiate with respect to N the maximum term*, designated here by Ξ_{\max} , obtained from the natural log, the grand potential. This maximum is found by setting the resultant equation to 0. The canonical ensemble term λZ is replaced by the fugacity†. Ignoring the translational change in the first schicht then:

$$0 = \frac{\partial \ln(\Xi_{\max})}{\partial N} = \ln(\tilde{p}) + \frac{\{E_a e^{-\theta} - \varepsilon\}}{kT} \quad \text{Equation 35}$$

In place of \tilde{p} substitute use P (since for most physisorption $\tilde{p} \approx P$.) and using molar quantities‡.

$$\frac{\bar{E}_a}{RT} e^{-\theta} = \frac{\bar{\varepsilon}}{RT} - \ln(P) \quad \text{Equation 36}$$

Now to evaluate $\bar{\varepsilon}$. As θ goes to infinity then P must go to P_{vap} . Thus, ε is the thermodynamic internal energy of vaporization at the temperature of the adsorbent (as well as the Gibbs' free energy, since $\Delta_l^a S = 0$) so $\bar{\varepsilon} = RT \ln(P_{\text{vap}})$, which defines a new the reference pressure, P_{vap} .

$$-\frac{\bar{E}_a}{RT} e^{-\theta} = -\ln(P_{\text{vap}}) + \ln(P) \quad \text{Equation 37}$$

$$-\frac{\bar{E}_a}{RT} e^{-\theta} = +\ln\left(\frac{P}{P_{\text{vap}}}\right) \quad \text{Equation 38}$$

What happens if θ goes to zero? In this limiting case, P must be finite. This is referred to as the threshold pressure with the symbol P_ζ .

$$-\frac{\bar{E}_a}{RT} = +\ln\left(\frac{P_\zeta}{P_{\text{vap}}}\right) \quad \text{Equation 39}$$

Thus, quantum mechanics predicts that there is a threshold pressure and violates “Henry’s Law” for physisorption. This further implies a phase change as discussed above, that is. the threshold pressure. This is the phase change must be to the liquid state and there is no requirement for a “break,” according to Guillet-Nicolas, Wainer, Marcoux, Thommes and Kleitz¹⁸, in the isotherm

* In other words, “What happens to the energy as the amount changes incrementally?”

† \tilde{p} is the latest IUPAC symbol for fugacity. Ideal gas and other ideal quantities are used throughout for simplicity. Obviously, these assumptions can be changed.

‡ The alternate IUPAC symbolism or overline (over bar) for molar quantities is used throughout due to confusion with subscript “m” which also stands for “monolayer.”

at higher pressure. However, such a break will be seen for mesoporosity where these “simple conditions” are not met*.

The solution for θ as a function of pressure is easy to obtain by substituting Equation 39 into Equation 38 and taking the \ln of the equation and rearranging:

$$\theta = -\ln \left\{ -\ln \left(\frac{P}{P_{\text{vap}}} \right) \right\} + \ln \left(-\frac{\bar{E}_a}{RT} \right) \quad \text{Equation 40}$$

Where if $\theta = 0$:

$$\ln \left(-\frac{\bar{E}_a}{RT} \right) = \ln \left\{ -\ln \left(\frac{P_\zeta}{P_{\text{vap}}} \right) \right\} \quad \text{Equation 41}$$

Then:

$$\theta = -\ln \left\{ -\ln \left(\frac{P}{P_{\text{vap}}} \right) \right\} + \ln \left\{ -\ln \left(\frac{P_\zeta}{P_{\text{vap}}} \right) \right\} \quad \text{Equation 42}$$

It is convenient to write this in a short form with the substitutions:

$$\chi = -\ln \left\{ -\ln \left(\frac{P}{P_{\text{vap}}} \right) \right\}, \quad \chi_\zeta = -\ln \left\{ -\ln \left(\frac{P_\zeta}{P_{\text{vap}}} \right) \right\} \quad \text{Equation 43}$$

So that the linearly transformed equation is obtained:

$$\theta = \Delta\chi \quad \text{where} \quad \Delta\chi := \chi - \chi_\zeta \quad \text{Equation 44}$$

The Equation 44 has been named the χ -equation from the letter that represent the function.[†]

Interpretation of χ and $\Delta\chi$ from the GCPF:

Both the plot of amount versus χ and $\Delta\chi$ present meaningful and easy interpretation of the data. The $\Delta\chi$ plot is a plot of the amount adsorbed versus the monolayer equivalence, whereas the χ plot yields the energy function, $\Delta^a \bar{\mathbf{E}}$.

$$\Delta_j^a \bar{\mathbf{E}} = -RT \exp(-\chi) \quad \text{or:} \quad \Delta_j^a \bar{\mathbf{E}} = -RT \ln(P/P_{\text{vap}}) \quad \text{Equation 45}$$

Thus, we arrive at the empirically supported isotherm by Polanyi²⁴⁻²⁷, by London²⁸ by DeBoer and Zwiiker²⁹⁻³¹, and by Fuller³²⁻³⁹.

* Whether this liquid phase is only in patches or is less dense microscopically than the bulk liquid cannot be determined from this derivation. (Indeed, quantum mechanics implies one cannot distinguish either between molecules or position. Only when the molecules are “frozen” due to the disturbance of an observation, will there be a distinction.) Regardless of details, it is obvious that macroscopically it is less dense than the bulk liquid. This is an interesting question that needs more research.

[†] The use of the letter comes from the handwritten X when we wrote the equation out. Since the BET used X and our cursive X looked like a χ we decided to call it that. There is nothing more to speculate about its selection.

A note about the energies: All the energies are negative*, that is adsorption is exothermic, and the energies are leaving the isothermal system in the form of heat. Another point is that the heat of adsorption in the calorimetry is $E_a^\ominus = \Delta_a^\ominus E + \varepsilon$, where $\varepsilon < 0$, so it is offset from the heat calculated from the isotherm and *Equation 45*.

The heat calculated is unlikely to be the measured isosteric heat of adsorption, where attempts are made to differentiate between two or more isotherms to get the values. This would be OK if one were to obtain very good data from the equations described here, but, of course, no one has done this[†].

Thus, for the “simple case” (homogeneous non-porous) everything is now defined:

For the overall areal density, one obtains n_a as a function of $\Delta\chi$ whose slope yields the n_m , the monolayer equivalence. The energy of adsorption, with the adsorbent vapor pressure at the temperature of the adsorbent as the reference state, as a function of χ through the starting energy E_a and the function $\mathbf{E}(\theta) = \Delta_a^\ominus \mathbf{E}(\theta) = E_a \exp(-\Delta\chi) < 0$. The standard Energy of adsorption is $\Delta_a \mathbf{E}^\ominus = \Delta_a^\ominus \mathbf{E}(\theta) + \varepsilon < 0$.

In part III a correction to the vapor pressure was introduced and used with the KJO data. It was noted in Part III that the correction of +0.01K made little difference in the answers, but it did make a difference in the standard deviation of the overall fit. This is the first modification to the “simple case.” Heterogeneity was also introduced. This correction involved the use of the “statistical area function” noted by the letter **Z**. This is seen only at very low pressures, so most of the literature does not have this recorded.

There are two other modifications to investigate. One is well understood, which is microporosity. The other is mesoporosity. Mesoporosity is not so well understood, but there are some parameters, using the **Z** function, which can be used to characterize the mesoporosity and perhaps relates back to the properties of porosity. These parameters indicate the position for the peak and width of the pore distribution. However, there is great uncertainty about the cause of hysteresis, which appears to be a very low energy process.

The equation $\mathbf{E}(\chi)/RT = -\exp(-\chi)$, χ -plot, is a representation of the energy and, thus, provides a method of determining where the mesoporosity should start and the shape of its distribution depending upon the adsorbent pore geometry and the surface tension of the adsorptive liquid. In the case of mesoporosity, with continued adsorption, the energy, $\mathbf{E}(\chi)$, continues to drop until the energy of the gas-liquid surface tension is reached, according to some geometrical appropriate equation, and the exothermicity of the pore filling is competitive with the quantum adsorption.

Microporosity and mesoporosity are the subject Part V and Part VI. Part V starts with the equations that are available from GCPF. Other topics, for which there is some preliminary

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Most literature values are given as positive and are therefore $\Delta_a^\ominus E$.

[†] To my knowledge, at least.

progress, is calculation of the calorimetric differential heat of adsorption and the binary adsorptive adsorption, will be discussed in Part VII considering the QM model.

The Schicht Equations:

Notice that in *Equation 42* the value of $\mathbf{exp}(-\Delta\chi)$ (or in the “simple case $\mathbf{exp}(-\theta)$ ”) varies from 1 for $\Delta\chi=0$, that is when there is no adsorbent, to 0 for $\Delta\chi = \infty$. Thus, this function is an indication, and can be proven to be so, of the “areal density” of the bare surface. or:

$$\theta_{\text{MT}} = \mathbf{exp}(-\Delta\chi) \Rightarrow \theta_1 = 1 - \mathbf{exp}(-\Delta\chi) \quad \text{Equation 46}$$

where θ_{MT} is the virtual “areal density” of the vacant first schicht and θ_1 is the area density of the adsorbate in the first schicht. Similar reasoning can be used to get the equations for successive layers to yield the series:

$$\begin{aligned} \theta_1 &= 1 - \mathbf{exp}(-\Delta\chi) \\ \theta_2 &= 1 - \mathbf{exp}(-\Delta\chi + \theta_1) \\ &\vdots \\ \theta_{n+1} &= 1 - \mathbf{exp}\left(-\Delta\chi + \sum_{m=1}^n \theta_m\right) \\ \Rightarrow \theta &= \sum_{m=1}^{\infty} \theta_m \equiv \Delta\chi \geq 0 \end{aligned} \quad \text{Equation 47}$$

The last equation can be proved, as a check on the derivation.

If the adsorption is restricted to one monolayer thickness, only the equation for θ_1 applies. This equation may be rearranged to yield the log-law, which is often observed.

$$n_{a,1} = n_m + \frac{n_m RT}{\bar{E}_a} \ln\left(\frac{P}{P_{\text{vap}}}\right) \quad \text{Equation 48}$$

Conclusion about the QM derivation

The evidence to the application of the QM picture for physical adsorption has so far been presented for the simple case in Part I through Part III. In the QM perturbation has been demonstrated in four different ways. It has also been shown that it is far superior to the discredited “Henry’s Law” isotherm equation, to which the BET and the Langmuir belong.

The QM is simple, but it may be that the subsequent addition of adsorbate molecules and the GCPT is a bit foreign to some. The exponential decay of the energy of adsorption seems to be a stumbling block for many, but never-the-less it has been an observation, without a reasonable explanation, since the early 20th century. From Polanyi and London to (early) Fuller, the recognition of the common trait was known but not adequately explained. Even after the QM discovery, the explanation was rejected repeatedly and an analogy explanation by Fuller¹³ had to be substituted just to get the experimental results into the literature.

The QM derivation of the basic χ -equation and use of χ -plots and $\Delta\chi$ -plots is an obvious step forward in the understanding of physical adsorption. While QM was being developed, another modern approach was being developed in Europe, which is today referred to as the Excess Surface Work (ESW.) There is a 1-to-1 correspondence between the two hypotheses, so everything that the QM presents is also applied to ESW. This is excellent agreement and mutual support for both hypotheses. A short section is presented here to explain how they are related

Disjoining Pressure and Excess Surface Work (ESW)

The main difference between χ and ESW hypotheses is that χ utilizes energy balance, whereas ESW utilizes the force balance. *Equation 49*

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 Kusakov¹⁹ and Derjaguin and Obukhov²⁰²¹ in 1936. It has for many years 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.

The equation for disjoining pressure is*:

$$\Pi_d = \frac{1}{A} \left(\frac{\partial G}{\partial z} \right) \Big|_{T,V,A} \quad \text{Equation 49}$$

Where Π_d is the disjoining press, z is the distance from the surface, A , and G is the Gibbs' energy. The equation for the ESW, excess surface work, Φ , is defined as[†]:

$$\Phi = n_a \bar{V} \Pi_d (n_a) \quad \text{Equation 50}$$

where \bar{V} (overbar or macron means molar) is the molar volume (IUPAC alternate designation.) Thus:

$$\Phi = -n_a \Delta_l^a \mu \quad \text{Equation 51}$$

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

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

Where Φ is the Surface Excess Work, Since $\Delta_l^a \mu$ is exothermic, Φ is endothermic.* Π_d has the following form as observed by B. V. Derjaguin and N. V. Churaev^{22,23}, but also by M. Polanyi^{24,25,26,27,†,‡} and with London,²⁸ deBoer and Zwikker,^{29,30,31,§} and by E. L. Fuller, Jr.^{32,33,34,35,36,37,38,39,**} et al. who demonstrated it was an exponential decay for the energy function. These precedents are used to make the functional form for Π_d , which has an exponential decay from the surface, where the half amount was later determined to n_m :

$$\Pi_d = \Pi_0 \exp(-n_a/\lambda) \quad \text{Equation 52}$$

$$\Delta_l^a \mu = \mu_0 \exp(-n_a/\lambda) \quad \text{Equation 53}$$

where from *Error! Reference source not found.* and *Error! Reference source not found.*, that H_0 relates to μ_0 by:

$$\Delta_l^a \mu = -\bar{V}\Pi \Rightarrow \mu_0 = -\bar{V}\Pi_0 \quad \text{Equation 54}$$

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

$$\Phi = -n_a \bar{V}H_0 \exp(-n_a/\lambda) \quad \text{Equation 55}$$

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

$$0 = -d\Phi(n_a)/dn_a = \bar{V}H_0 \left\{ \exp(-n_a/\lambda) - \frac{n_a}{\lambda} \exp(-n_a/\lambda) \right\} \quad \text{Equation 56}$$

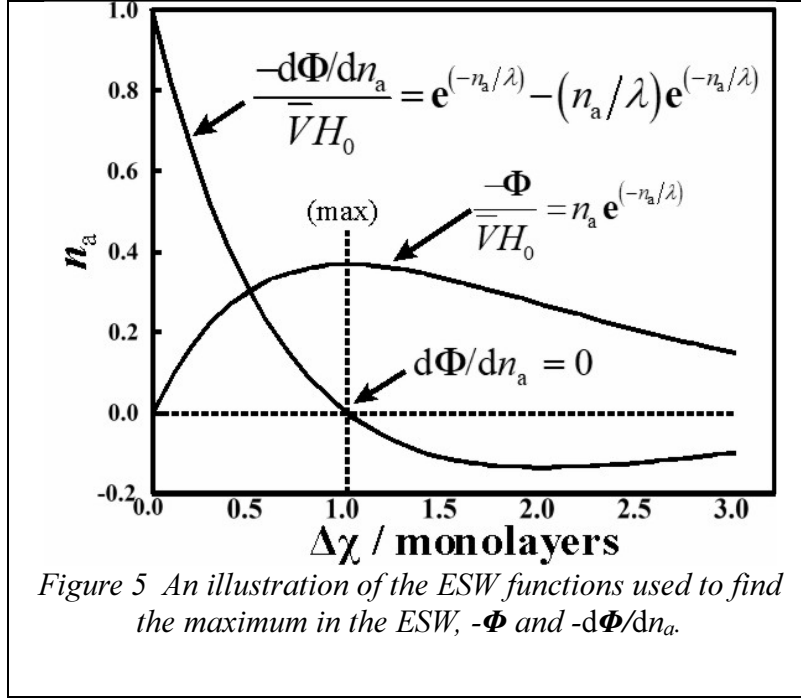
* Negating it is positive, that is, it takes work to remove the material from the surface.

† 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 “vap”] 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.



The $\Delta_i^a \mu$ is the change in the chemical potential transforming from the bulk liquid adsorptive to the adsorbate at the temperature of the adsorbent. Adolphs^{40, 41, 42, 43, 44} et al., related to the adsorptive/adsorbate to the chemical potential of Equation 44 which is related to the adsorptive pressure by:

$$\Delta_i^a \mu = -RT \ln(P/P_{\text{vap}}) \quad \text{Equation 57}$$

Eliminating the chemical potential between Equation 53 with Equation 57 yields the pressure dependence of the ESW formulation:

$$-RT \ln(P/P_{\text{vap}}) = \bar{V} \Pi_0 \exp(n_a/\lambda) \quad \text{Equation 58}$$

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

$$-\ln \left\{ -\ln \left(\frac{P}{P_{\text{vap}}} \right) \right\} = -\ln \left(\frac{\bar{V} \Pi_0}{RT} \right) + \frac{n_a}{\lambda} \quad \text{Equation 59}$$

This then is identical to the χ -equation with:

$$E_a = -\bar{V} \Pi_0 \quad \text{and} \quad \lambda = n_m \quad \text{Equation 60}$$

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 χ -plot abscissa is a plot of energy, as $\ln(E/RT)$. Obviously, these plots are predicted by ESW as well. The ESW has another plot to yield the monolayer equivalence illustrated in Figure 5.

Conclusion about the QM derivation

The evidence to the application of the QM picture for physical adsorption has so far been presented for the simple case in Part I through Part III. In the QM perturbation has been demonstrated in four different ways. It has also been shown that it is far superior to the discredited “Henry’s Law” isotherm equation, which the BET and the Langmuir belong.

The QM is fairly simple, but it may be that the subsequent addition of adsorbate molecules and the GCPT is a bit foreign to some. The exponential decay of the energy of adsorption seems to be a stumbling block for many, but never-the-less it has been an observation, without a reasonable explanation, since the early 20th century. From Polanyi and London to (early) Fuller, the recognition of the common trait was known but not adequately explained. Even after the QM discovery, the explanation was rejected repeatedly and an analogy explanation had to be substituted just to get the experimental results into the literature.

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For micropores, the most convenient plot is the log-law. For mesoporosity it seems that the ESW plots are more straight forward by modifying Φ with the Kelvin equation or some other equation that seems appropriate. The QM approach adds a generalized distribution to the basic χ -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 χ -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.

Conclusion Concerning ESW

The force approach called ESW is as powerful as the QM analysis but has not been presented with so many implication as of the moment. It seems to have promise to be able to handle the hysteresis problem, certainly as good if not better than the QM approach. Development is in progress;

Appendix I – the Dubinin "thermodynamic criterion"

Polanyi^{24,25} and with London²⁸ 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 61*.

$$A := \mu_a - \mu_l = RT \ln(P_{\text{vap}}/P_a) \quad \text{Equation 61}$$

This leads to the Dubinin-Radushkevich⁴⁵ equation for which Kaganer⁴⁶ applies to the non-porous surfaces. The isotherms and some others in this classification fit the χ -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 62 for the dependence of A on temperature

$$\frac{\partial A}{\partial T} := \frac{\partial \Delta_l^a \mu}{\partial T} = 0 \quad \text{Equation 62}$$

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:

	$\therefore \Delta_l^a \mathbf{S} \approx 0 \Rightarrow \therefore \Delta_l^a \bar{\mathbf{E}} \approx RT \ln(P_{\text{vap}}/P)$	<i>Equation 63</i>
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See also Bering and Serpinski⁴⁷ and Bering, Dubinin and Serpinski⁴⁸ for further discussion of the thermodynamics and approximations leading to *Equation 63*. This equation forces the question, "Where is the transition to the liquid state." Brunauer's answer to that question the Fuller posed was that it was at $P/P_{\text{vap}} = 1$, consistent with Brunauer's writings⁴⁹, and that it was not visible due to the experimental and other problems. However, if the transition is not near P_{vap} , then it must be when P approaches 0, otherwise, *Equation 63* predicts the energy goes to infinity as $P \rightarrow 0$.

Adamson⁵⁰ observed that the $\ln(-\ln(P/P_{\text{vap}}))$ was the best empirical equation transform, but criticized it, quoting Brunauer⁵¹,* on theoretical grounds[†] and the lack of v_m being explicit in the equation.

The eventual importance of *Equation 63* became apparent with Fuller's observation that the internal energy, $\Delta_l^a \mathbf{E}$ was exponential decay function of coverage. This observation had been

* 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

noticed by others, 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 II The “distributions”:

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 64+*.

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

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

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

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

Equations 64+ The equations for function **N**, **D** and **Z** that are used consistently for publications by Condon.

Appendix QM symbol list

\hbar = the reduced Plank's constant

Ψ = (time dependent) wave function(s)

ψ = time independent wave function(s)

ψ^* = the complex complement of ψ .

$\hat{\mathbf{H}}$ = the Hamiltonian

E = the energy from the bottom of the well

monolayers. Brunauer did not assume dense layers in his BET hypothesis, why is this disallowed for other hypotheses?

$\langle |$ and $| \rangle$ = bra and ket

\mathbf{U} = the unit step function

A = the aliquot limiting area

a = the admolecules cross sectional area.

β = an energy defined with the GCPF

ε = the energy of vaporization of the adsorptive at the temperature of the adsorbent = $\Delta^a \mathbf{E}$

E_1 = the base energy of the well after the first molecule has been adsorbed

E_n = the base energy of the well after the n^{th} molecule has been adsorbed

N = the total number of admolecules

$\theta = aN/A$

$\mathbf{E}(N)$ = the energy as a function of total number of molecules.

$\theta_{\text{MT}} = 1 - \theta_1$

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Data and materials availability:

All the data and materials are available in the open literature and are referenced herein.

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