

Equivalency of the Dubinin-Polanyi Equations and the QM Based Sorption Isotherm Equation - Part A, Mathematical Derivation.

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Abstract:

It is demonstrated that the most widely used sets of the Dubinin-Polanyi (DP) isotherm equations may be derived from an isotherm equation that has its basis in simple quantum mechanical (QM) assumptions. These derivable isotherms include the Dubinin-Radushkevich (DR), the Dubinin-Astakhov (DA) and the Dubinin-Radushkevich-Kaganer (DRK) equations. The initial derivation in part A assumes no energy distributions other than that obtained in the QM treatment. Using this homogeneous assumption the DR, DA and DRK equations were found to be valid within 2% over a pressure range that covered at least a factor of 100 for typical ceramic adsorbents. In the course of the derivation, the philosophical problem of dual use of the DR equation for both porosity and open surfaces (DRK equation) is resolved. The methodology for heterogeneous surfaces and comparisons to DP and other isotherms using the heterogeneous assumption are described in part B.

Key words:

Adsorption, Porosity measurements, Physical adsorption, Isotherms, Physisorption

1. Introduction:

The purpose of this and the following article is to demonstrate that the Dubinin-Polanyi (DP) isotherm equations and a quantum mechanically derived adsorption isotherm are mathematically the same over the pressure ranges normally used experimentally. By doing this, two objectives are accomplished:

- 1) the validation of the DP description by placing on more firm theoretical foundations and
- 2) the demonstration of the usefulness of the QM/statistical mechanical derivation, and the P description, in that it is now strongly supported by extensive experimental data which has been analyzed using the DP equations.

In this part (part A) a homogeneous surface is assumed in the derivation. This yields a mathematical proof of the equivalencies. In part B, the heterogeneous assumption is examined. The heterogeneous assumption requires some assumptions about surface energy distributions. Numerical calculations along with some reasonable distribution assumptions demonstrate a much broader range of validity between the two representations.

The DP isotherm equations (as described by Dubinin[1],[2], Dubinin and Stoekli[3], Huber and Stoekli[4] and Stoekli[5] plus many more references) in the various forms are used extensively to analyze porosity of materials. These equations are no doubt the most widely used of the analytical forms for adsorption isotherms for porous materials. There are several modifications, but the isotherms used most often are the Dubinin-Radushkevich[6],[7] (DR) and the Dubinin-Astakhov[8],[9],[10] (DA) equations. Another isotherm, the DRK equation, originally proposed by Kaganer[11],[12] to overcome the break-down of "Henry's law," is identical to the DR equation in form but is applied to surface area measurements other than porosity. The use for this application seems to some investigators as a curious phenomenon; i.e., an isotherm that is derived for porosity is used in an unrelated area.

The DR and DA equations, originally found by Dubinin and Radushkevich[13] to be very good empirical fits to adsorption data in porous carbon and zeolites, were later derived by Dubinin based upon two assumptions. The first assumption made by Dubinin[14] is the "thermodynamic criterion" which is supported by many experimental observations. This criterion utilizes the concept of adsorption potential, A , and is given as

$$\left[\frac{\partial A}{\partial T} \right]_{\theta} = 0 \quad (1)$$

where

$$A = RT \ln \left(\frac{P_s}{P} \right) \quad (2)$$

Here P_s is the vapor pressure of the adsorbative that would be observed over the liquid phase that has a flat interface with the gas and P is the actual adsorbative pressure. (Due to the large number of symbols used in this article, a list of all symbols, SI and otherwise is given in Appendix A.) The second assumption presented by Dubinin[14] is that the energy of adsorption between the adsorbate and the surface follows a Weibull distribution curve. From this the generalized DA equation is derived, of which the DR equation is a special case. One form of the DA equation is:

$$\ln \left(\frac{n_A}{n_{Ao}} \right) = B \left(\frac{T}{\beta} \right)^k \ln^k \left(\frac{P_s}{P} \right) \quad (3)$$

In this equation k is a constant whose value can vary somewhat, usually from 1.5 to about 4. (The symbolism has been changed here somewhat to conform with the 1989 SI/IUPAC conventions.) The special case with k equal to 2 is the DR equation. The parameter β is dependent upon the adsorbate; whereas, the energy term B is dependent upon the adsorbent. The subscript A indicates the adsorbate. The n_{Ao} is the number of moles to completely fill the pores of the adsorbent. For this purpose, a corrected density of the liquid is used. This correction is dependent upon where in the isotherm the pore filling begins. Dubinin, Zhukovskaya and Murdmaa[15] (DZM) presented a tabulation of the corrected densities. It is also possible to calculate density from the QM based equations. The external, non-porous area is assumed to be very small relative to the pore volume and may therefore be ignored. The DRK equation is identical in form to the DR equation, i.e. $k = 2$, with n_{Ao} becoming n_m , the monolayer equivalent moles adsorbed.

The quantum mechanical (QM) based isotherm derived by Fuller and Condon[16] from which the DP equations may be derived is based on the following assumptions.

- (1) The surface may be treated as a quasi-two dimensional (2D) potential box (i.e. the potential difference is only normal to the surface, the 2D of the surface is the box dimensions) of a size considerably larger than an individual adsorbate molecule. The surface may consist of patches of individual planes as assumed by Sanford and Ross[17].
- (2) The first particle adsorbs and takes the QM form of a 2D ideal gas, i.e. a simple particle in the box.

- (3) The second particle adsorbs as another QM particle in the box. This box, however, has been modified by the first particle. The potential well now looks like the original with a "tooth" present where the first particle is located. It is therefore assumed that the energy of attraction of the bare surface is greater than with the "tooth". This "tooth" then is a classical approximation for the location of the first particle.
- (4) The third adsorbate molecule adsorbs as the second except there are now two "teeth". Classically, these "teeth" are normally, just by statistical considerations, not in the same location. However, occasionally they will coincide and become effectively one "tooth." In the case of only two adsorbate molecules this will be extremely rare, but it becomes more common as the surface coverage increases. This effect is taken into account naturally by the QM treatment. Subsequent adsorbate molecules follow the same pattern.

A bit of explanation is in order about the energies involved in this system. The energy difference between the top of the potential box and the bottom without any particles present would normally be referred to as the adsorption energy. Once the first two particles are present, in addition to the attraction to the surface, there exists an energy of interaction between the first and second molecules. This energy of interaction is the same as that between two molecules in the liquid state. Thus, this difference between the energy at the outside of the box (i.e. gas phase) and the top of a tooth is the same as the energy of attraction between two liquid molecules.

- (5) The translational energy of the particles adsorbing are considerably above the ground state level and the formation of the solid phase is not possible.

This condition leads to the sixth condition by the following reasoning. The location of the tooth within the adsorbent patch would be important if the quantum number of the second adsorbate molecule were low, that is if the wavelength of the particle were not much smaller than the tooth. If it is not much smaller than the tooth, it however implies that the translational energy is close to the ground state in violation of assumption (5). A rough calculation of a typical adsorption system is enough to demonstrate this. The average particle has a very high quantum number since $kT \gg h^2/8mx^2 = \epsilon_t$. For example, even for very small adsorbent patches, say 10 nm, and liquid N₂ adsorbate, $kT = 1 \times 10^{-21}$ J and $\epsilon_t = 2 \times 10^{-26}$ which gives an $\langle n_x \rangle = 400$. For N₂ an average n_x of 20 represents a sufficiently small wavelength, i.e. 0.5 nm compared to the nitrogen molecule of ~4 nm, to assume that the tooth position is not very critical. The perturbed potential well energy under these assumptions becomes an average over the entire area, which includes the tooth/teeth.

- (6) Since the average wave length of the adsorbate particles is very short compared to the molecular size, the entire treatment may be done classically provided the conclusion about the energies obtained in the QM treatment is used.

From the above considerations, it would appear that the number of states available for a typical adsorption temperature are considerably greater than the number of particles. Therefore:

- (7) The system is then assumed to be a dilute system (of filled states not particle concentration) for which Maxwell-Boltzmann statistics applies. However, there is only one "box" in which to put all the adsorbate particles. From this then, the grand canonical partition function is derived to arrive at the QM based isotherm equations.

The results for the energies *appear* classically *as if* the first adsorbate molecule "shields" an area of the surface from the second adsorbate molecule, and so forth for subsequent adsorbates. (For this reason, Fuller refers to this as autoshielded physisorption or ASP.) Added to this are the interparticle interactions. The use of a uniform potential box is the recognition of the fluid-like nature of the adsorption. Fluid-like implies that there are no adsorption sites and no localized bonds of localized intermolecular forces. This condition might be too extreme as it appears that adsorbates for which directional forces are expected, such as water, appear to fall within the model.

The shielding obtained by the classical derivation in terms of energy can be derived using the WKB approximation as given in Appendix B. The resultant equation as derived in Ref. [16] for only one energy patch (one "box") is:

$$\frac{n_A}{n_m} = (\chi - \chi_c)U(\chi - \chi_c) \quad (4)$$

where U is the unit step function and χ and χ_c are defined by:

$$\chi \equiv -\ln\left(\frac{A}{RT}\right) \quad (5)$$

and

$$\chi_c \equiv -\ln\left(\frac{E_a}{RT}\right) \quad (6)$$

where E_a is the energy released for the first molecule adsorbed compared to the liquid state¹. Eq. (4) will be referred to here as the chi (χ) form of the QM isotherm equation, or the (simple) χ equation. It will be convenient to define the quantity $\theta = \frac{n_A}{n_m} \frac{P}{P_c}$ to simplify the equations. Using the symbol θ for n/n_m this yields the very simple looking equation:

$$\theta = \Delta\chi U(\Delta\chi) \quad (7)$$

The left side of this equation is related to the amount adsorbed, whereas the right side relates to the energy considerations. This equation will be used to link the functions which follow in order to derive the DP equations.

Given the isotherm relationship of adsorption pressure versus amount adsorbed, Eq. (7) can be used to analyze for both the surface energy and surface area for nonporous materials. Fuller, *et. al.*, have done precisely this for a variety of materials. These materials included, for example, lunar soils[18],[19], thoria[20], diamond and alumina[21] and other ceramics[22],[23],[24],[25]. Fuller also demonstrated that this curve could be used as a convenient substitute for the comparison plots[26],[27], circumventing the errors associated with the standard curves.

This author's experience in the analysis of zeolite data indicates that the data fits to the DP equations with the χ isotherms modified for porosity are seldom distinguishable by

¹ Note that E_a is defined with as a positive value which is the negative of the energy for the adsorption process. This is the convention adopted by Fuller; whereas, the adsorption energy defined by Dubinin is a negative value.

statistical methods. Tests such as the F-test have usually failed to yield a distinction. Occasionally the P fit was better but this was often due to slight amounts of external surface area which the DR and DA equations do not address. The reason for this indistinguishability is now quite obvious, since the DA, DR and DRK equations can be derived from P theory. The derivation presented here will not seem straight-forward to some who are unfamiliar with modern mathematical proofs. It is, however, much simpler to understand, and present, than a more linear-thinking derivation. It is not uncommon today in mathematics to approach a proof from two results to arrive at the equivalence at some middle point, which is done here.

In the following derivations the methodology is to:

Step 1 - show the equivalency between the chi formulation and the DP formulation for surfaces which have no curvature,

Step 2 - correct the energy term for surface curvature.

Step 3 - correct for geometrical restrictions.

Step 4 - combine the two corrections into the method described in step 1.

In this paper, the corrections for step 2 and 3 are both performed for cylindrical geometries. The geometry which assumes slit shapes is much simpler since it requires step 3 but not step 2.

Step 1 - derivation using P equation without surface curvature corrections: Some preliminary mathematics is needed before the derivation of the DR and DA equations can be demonstrated. Two functions are used in this derivation which are related to each other over a particular range. These two functions are defined here as:

$$f_1(x) \equiv Qe^{-kx} \quad (8)$$

and

$$f_2(x) \equiv \ln(x) \quad (9)$$

In relation to P theory, the Q portion of Eq. (8) will be given as:

$$Q = \left(\frac{E_o}{RT} \right)^k \quad (10)$$

Both functions, f_1 in Eq. (8) and f_2 in Eq. (9), can be approximated by a series expansion, but the point about which they can be expanded must be carefully selected. If one sets up a parametric relationship² for these equations of the form:

$$f_2(x) = sf_1(x) + b \quad (11)$$

Then an inflection point is centered on $x = 1/k$. Using the series expansion about $1/k$, one obtains the following for s (slope) and b (intercept) (also: $e = 2.718...$):

² I.E. if one has two linear equations with a common independent variable, a third linear equation between the dependent variables may be determined.

$$s = -\frac{e}{Q} \quad \text{and} \quad b = 1 - \ln(k) \quad (12)$$

Notice that b is a function of k . It is also useful to know over what range of values one can use this relationship without a significant error. Expanding the series does not do a proper job of yielding this answer since the two series do not converge at the same rate. However, one can compare the Taylor series expansion from Eq. (8) and that from Eq. (9) directly to Eq. (11) to determine this. (Alternatively a few sample calculations yield the answer.) For a 2 % error in the value of x compared to the range considered, the range is from $x = 0.5/k$ to $1.5/k$. (This range can be expanded considerably if one recalculates s and b for the entire range considered. This will be more important for the equations related to porosity below. For the moment, the estimates from Eq. (12) will be used.)

The above relationship, Eq. (11), may be used to relate P theory for a flat surface to the DP isotherm. Eq. (8) may be associated with the pressure. Thus, using the definition of θ :

$$f_1(\Delta\chi) \equiv \left(\frac{E_o}{RT} e^{-\Delta\chi} \right)^k = \ln^k \left(\frac{P_s}{P} \right) \quad (13)$$

Substituting in the x range given above into this equation yields the ratios of the upper and lower limits of pressure for which the 2 % error criterion applies. For a typical ceramic material with a P_c of -2.5, this corresponds to a factor of 100 in the pressure range. Since for a flat surface Eq. (7) states that $\theta = 2$ when $\theta > 0$, then equation substitution into Eq. (9) may be used to yield:

$$f_2(\Delta\chi) = \ln(\theta) \quad (14)$$

These substitutions yield:

$$\ln(\theta) = -\frac{e}{Q} \ln^k \left(\frac{P_s}{P} \right) + 1 - \ln(k) \quad (15)$$

or with \log_{10} as normally seen in the literature:

$$\log(\theta) = \left[-\frac{2.3026^{(k-1)}e}{Q} \right] \log^k \left(\frac{P_s}{P} \right) + \left[\frac{1}{2.3026} - \log(k) \right] \quad (16)$$

Q is the energy term given in Eq. (10). This is exactly the form of the DP as would be applied to a flat surface. With $k = 2$, this is referred to as DRK equation proposed by Kaganer[10]:

$$\log(n_a) = A \log^2 \left(\frac{P_s}{P} \right) + \log(n_b) \quad (17)$$

Where the intercept yields, n_b , assumed to be the value for monolayer equivalent. This in turn yields a value for the surface area. From the above equation, however, one can determine that the relationship between the monolayer coverage, n_m , and the intercept value, n_b , is:

$$n_m = n_b e^{-(1 - \ln(k))} \quad (18)$$

or for the DRK equation, $k = 2$:

$$n_m = 0.736n_b \quad \text{for } k = 2 \quad (19)$$

The isotherms associated with the porosity may be derived in a fashion similar to that used in this section. To do this, Eq.(8) and Eq. (9) need to be modified. Eq. (8), which has been associated with the fugacity, will incorporate the surface tension correction. Eq. (9) which relates the adsorbate activity with the amount adsorbed, is modified to account for the limitations of geometry. These modifications depend upon the specifics of geometry selected. For this purpose, a geometry of long cylindrical pores is used since this is probably the most common application.

Step 2 - modification of the energetics due to surface curvature: The energetics due to surface curvature is derived using classical thermodynamics combined with the equations of state given by the chi equations. The caveat to this approach is that most pores considered are very small and there is always a question of the applicability of macroscopic equations being applied to a microscopic phenomenon. This problem is common when addressing surface problems. Compared to the gas-adsorbate surface, the surface considered here, the solid - adsorbate surface, statistically involves more particles, counting the solid surface atoms. This question could be a good area of future theoretical research, but for the moment the classical approach to this problem will be utilized.

One of the equations utilized in the derivation of the energetics is the expression for the spreading pressure. This is obtained using the Gibbs-Duhem equation with the results the isotherm obtained in chi theory (see Appendix C for details.) The relevant equation is:

$$\gamma_a - \gamma_\infty = -\frac{(\Delta\chi + 1)}{A_m} \ln\left(\frac{P}{P_o}\right) \quad (20)$$

The energy correction for the curved solid surface is based on the Kelvin equation and the surface tension (Eq. (20)) of this interface. For the adsorbate-solid cylindrical interface the Kelvin equation would be:

$$-RT \ln\left(\frac{P_o}{P_s}\right) = + \frac{(\gamma_a - \gamma_\infty)V_m}{r} \quad (21)$$

where r is the radius of curvature of the adsorbate-adsorbent surface and the plus sign emphasizes that this is for a concave surface. (Note that in this macroscopic approximation, the location of the adsorbate-adsorbent surface is the same as the solid surface. Thus r will be used for the pore radius as well.) In most presentations of the Kelvin equation, the vapor pressure over the curved surface is given the symbol P_o and P_s is the vapor pressure over the flat surface, i.e. the experimentally observed, normal vapor pressure. This convention is continued in this article. The surface being considered here is the adsorbate-solid interface, and this surface has only one radius of curvature. This is the radius of the cylinder. (For enhanced pore filling due to the surface tension of the liquid-gas interface, there are two.) Also notice that the tension used is $(\gamma_a - \gamma_\infty)$. If the surface is totally covered with the dense bulk liquid, there should be no net tension difference as this term correctly yields. One can substitute Eq. (20) into Eq. (21) to obtain the following equation:

$$\ln\left(\frac{P_o}{P_s}\right) = \frac{V_m}{rA_m}(\Delta\chi + 1) \ln(P/P_o) \quad (22)$$

P and P_c are referenced to P_o , the diminished vapor pressure due to the surface curvature, and not to P_s . In other words, P is the value that would be obtained for the flat surface. This equation indicates the interesting result that P_o is a function of P . There is *no contradiction* here: it is perfectly permissible for P_o to be a function of P , but P_s may not be. Two extremes for this equation are instructive. As the pressure, P , approaches P_o , the P_o approaches P_s thus:

$$\lim_{P \rightarrow P_o} \ln\left(\frac{P_o}{P_s}\right) = 0 \quad , \text{ i. e. } P_o \rightarrow P_s \quad (23)$$

Classically, this is what would be expected, as this approaches a fully covered first layer (plus other layers), and thus, there would be no extra energy due the interaction with the solid surface. The other extreme is as the P approaches zero:

$$-\ln\left(\frac{P_o}{P_s}\right) \rightarrow \left(\frac{E_a}{RT}\right) \frac{V_m}{rA_m} \quad (24)$$

For a cylindrical pore, the smallest radius would be V_m/A_m , or twice the molecular radius. Thus the lower limit as r approaches V_m/A_m is:

$$\lim_{\Delta\chi \rightarrow 0} \ln\left(\frac{P}{P_s}\right) = \lim_{\Delta\chi \rightarrow 0} \ln\left(\frac{P}{P_o}\right) + \ln\left(\frac{P_o}{P_s}\right) = 2\left(\frac{E_a}{RT}\right) \quad (25)$$

This is precisely the relationship that Fuller, *et. al.*[28], determined experimentally for several microporous adsorbents. Referencing P to P_s , i.e., the experimental saturation pressure, yields the dependence of the P equation on the surface curvature above the unit step function criterion:

$$\ln\left(\frac{P}{P_s}\right) = \left(1 + \frac{V_m}{rA_m}(\Delta\chi + 1)\right) \left(\frac{E_a}{RT}\right) e^{-\Delta\chi} \quad (26)$$

It will be convenient to group the energy term with the pressure in order to utilize Dubinin's adsorption potential and rearrange Eq. (26):

$$\frac{A}{E_a} = \left(1 + \frac{V_m}{rA_m}(1 + \Delta\chi)\right) e^{-\Delta\chi} \quad (27)$$

Where A is still referenced to P_s as applied in the DP formulations. The experimentally observed pressure relationship is no longer P/P_o , but rather P/P_s . This could be a source of confusion. A clear distinction must be made between the P plot based upon P_o and the observed P plot which is referenced to P_s . For the observed P plot the notation P_{obs} will be used and is defined as:

$$\chi_{obs} \equiv -\ln(-\ln(P/P_s)) \quad (28)$$

The definition for P (without subscripts) remains unchanged. The definition for P_c likewise remains unchanged and a similar definition of $P_{c,obs}$ to Eq. (28) is used. For porous materials the " P plot" obtained experimentally, actually P_{obs} , will likely differ

from the plot based upon P value. To convert P_{obs} to P for a concave surface one could first determine P_c by:

$$\chi_c = \chi_{c,obs} + \ln \left(1 + \frac{V_m}{rA_m} \right) \quad (29)$$

and then determine P using multiple approximations of the equation:

$$\chi = \chi_{obs} + \ln \left(1 + \frac{V_m}{rA_m} (1 + \Delta\chi) \right) \quad (30)$$

A useful approximation at low pressure, and thus low P , is to combine Eqs. (29) and (30) and expand the ln term to yield:

$$\Delta\chi_{obs} = \frac{\Delta\chi}{1 + V_m/rA_m} \quad (31)$$

Notice that if there are two or more different pore sizes, the P plots no longer add. Under these conditions, it is the P_{obs} plots which add. Unfortunately, this complicates the calculations.

The question: "At what pore size may one confidently ignore the curvature effect?" can be answered by inspection of Eq. (27). If the data are good to within 1%, then a $rA_m \neq 0.01V_m$ is required, well into what is normally considered the macropore range.

By

inspecting the implications for the concave surface it will be convenient to define f_1 , the function associated with energy terms, by the following equation:

$$f_1(\Delta\chi, r) \equiv \left(\frac{A}{E_a} \right)^k = \left(1 + \frac{V_m}{rA_m} (1 + \Delta\chi) \right)^k e^{-k\Delta\chi} \quad (32)$$

The function f_2 , the function associated with the physical coverage, is also modified but by the geometrical restrictions associated with the pores.

Step 3 - geometrical restriction: The general approach to the restrictive geometry problem is similar to that presented by several other investigators. Apparently, the first to point out the restriction and use it to calculate the porosity were Barrett, Joyner and Halenda (BJH) [29]. There is one additional feature to this treatment that is required and that feature is the variation of the density of the adsorbed phase, as pointed out by DZM [15]. For illustration, their data is presented in Table 1. From these density measurements alone, an estimate of pore size may be made from the P density calculation. This is done by assuming that the pore filling as reported was a sharp cut-off in the uptake of the adsorbent. This is only a crude estimate partly due to the pores continuing to fill somewhat after the geometrical constraint is reached due to densification of the adsorbate. Furthermore, the estimate assumes no geometrical shape, i.e., the geometry would be equivalent to slits. This should become clearer with the derivation below. This density variation effect may be calculated from the P equations in the following fashion. (It's better to start from the P equation point of view than from Dubinin's revelation in order to be consistent here in the derivation. Dubinin's revelation, of course, predates the P derivation.)

The P theory assumes, for a first approximation, that the interaction between adsorbing molecules are all of the same energy. That is, the intermolecular force between a

molecule in the second layer and the first layer is the same as between a molecule in the third and second layer. This may be an oversimplification, but this assumption is used by most numerical and other modeling techniques including the BET [30] and the BDDT [31] isotherms. With this assumption, there is no particular reason that the *areal density*, defined as mass or moles per unit area, of molecules in the second, third, etc. layers should differ. However, the P theory makes no assumption about layers, indeed it treats all adsorbed molecules equally. The areal density that can be derived from the P theory is that of the adsorbed molecules which at any one time are immediately in contact with the surface, i.e. the shielding molecules or in the QM description the "teeth". The density of this layer (on a flat surface) compared to liquid density, z_1 , is given by the equation [16]:

$$\theta_1 = 1 - e^{-\Delta x} \quad (33)$$

Thus, if an equivalent monolayer of gas is adsorbed, the areal density is only 0.632 of that expected from the liquid density. How the difference in density is accomplished is not specified in the P theory. This could be patch-wise adsorption or merely that the adsorbate is less dense than the bulk liquid. It is known that if the adsorption energy is high enough, a regular pattern of adsorption patches may form. (e.g. see Ref [32]). With low adsorption energy, a more random adsorption takes place.

A common way of viewing pore filling is to utilize the "thickness" (as defined by deBoer, et. al. [33]) of a layer, t . This thickness is known to be an average thickness, as the multilayers do not stack perfectly. This average thickness, however, is dependent upon the adsorbate density, which is known from DZM to deviate from the liquid density. The only difference in density as noted above is in the plane of the surface and not normal to the surface. Thus, the areal density correction for the first layer is also the adsorbate density correction. Using this correction t is related to z (on a geometrically unrestricted surface) by:

$$\theta = \frac{tA_m(1 - e^{-\Delta x})}{V_m} \quad (34)$$

or an average volume of the adsorbed layer by:

$$\theta = \frac{VA_m(1 - e^{-\Delta x})}{A_s V_m} \quad (35)$$

The equations derived which express the geometrical restriction are straight-forward geometry [29]. The volume adsorbed in a cylindrical pore of length l and radius r is given in terms of adsorbate thickness by:

$$V_{\text{cylinder}} = \pi(2rt - t^2)l, \quad t \leq r \quad (36)$$

$$V_{\text{cylinder}} = \pi r^2 l, \quad t \geq r$$

This is to be compared to an equivalent flat surface of dimensions l by $2Br$.

$$V_{\text{flat}} = 2\pi r t l \quad (37)$$

Since this is not a flat surface, a more general approach is to use P in place of z in Eq. (34) and Eq. (35). According to the BJH formulation, the actual value of z must take into account the fact that some of the material that would normally be adsorbed on

a flat surface with volume given by Eq. (37) is not present according to Eq. (36). Thus the experimental θ will be related to θ_P by:

$$\theta = \frac{V_{\text{cylinder}}}{V_{\text{flat}}} \Delta\chi \quad (\text{for } \Delta\chi > 0) \quad (38)$$

The thickness is then related to θ_P through the areal density function by the relationship derived from Eqs. (34) and (7) above the unit function criterion:

$$t = \frac{V_m \Delta\chi}{A_m (1 - e^{-\Delta\chi})} \quad (39)$$

Using Eqs. (36), (37), (38) and (39) yields:

$$\theta = \Delta\chi - \frac{V_m \Delta\chi^2}{2rA_m (1 - e^{-\Delta\chi})} \quad \text{if } \Delta\chi \leq \frac{rA_m}{V_m} (1 - e^{-\Delta\chi}) \quad (40)$$

or:

$$\theta = \frac{rA_m}{2V_m} (1 - e^{-\Delta\chi}) \quad \text{if } \Delta\chi \geq \frac{rA_m}{V_m} (1 - e^{-\Delta\chi}) \quad (41)$$

Making substitutions into Eqs. (40) and (41) in Eq. (9) yields a new function, f_2 . The function f_2 is now dependant on r :

$$\begin{aligned} f_2(\Delta\chi, r) &\equiv \ln(\theta) \\ &= \ln(\Delta\chi) + \ln\left(1 - \frac{V_m \Delta\chi}{2rA_m (1 - e^{-\Delta\chi})}\right) \\ &\quad \text{if } \Delta\chi \leq \frac{rA_m}{V_m} (1 - e^{-\Delta\chi}) \end{aligned} \quad (42)$$

or:

$$\begin{aligned} f_2(\Delta\chi, r) &\equiv \ln(\theta) \\ &= \ln(1 - e^{-\Delta\chi}) - \ln\left(\frac{2V_m}{rA_m}\right) \\ &\quad \text{if } \Delta\chi \geq \frac{rA_m}{V_m} (1 - e^{-\Delta\chi}) \end{aligned} \quad (43)$$

Step 4 - combining energy considerations and geometrical restrictions: The Taylor series expansions about $\theta_P = 1/k$ may be carried out as before. Notice that except for some additional linear terms, Eq. (32) is similar to Eq. (13) and Eq. (42) is similar to Eq. (14). The functions, f_1 and f_2 , may be related as before with new numbers. Thus:

$$f_2(\Delta\chi, r) = s' f_1(\Delta\chi, r) + b' \quad (44)$$

Where in addition to b' being a function of k , both s' and b' are functions of r . It should be noted that to apply θ_P theory, r should be greater than V_m/A_m for cylinders.

Physically, the smallest value for r is $0.5V_m/A_m$; i.e., when the pore radius and the adsorbate molecule radius are equal. Chi theory, however, requires that the molecules are able to pass by each other, thus the lower limit of V_m/A_m . (Another function must be used in place of e^{-P} when the molecules cannot pass each other. This function, however, can be roughly approximated by e^{-P} to yield nearly the same answer.)

As the pore sizes get large, the relationship approaches the constants given for the flat surface. Following the method outlined previously, the following equation is determined by substituting into Eq. (44):

$$\log(\theta) = 2.303^{k-1} s' \left(\frac{RT}{E_a} \right)^k \log^k \left(\frac{P_s}{P} \right) + \frac{b'}{2.303} \quad (45)$$

Which is the DR and DA equations. By comparison of Eq. (42), Eq. (32) and the same inflection point the values of s' and b' are:

$$s' = - \left(1 + \frac{V_m}{rA_m} \left[1 + \frac{1}{k} \right] \right)^{-k} e \quad (46)$$

and

$$b' = 1 + \ln(k) + \ln \left(1 - \frac{V_m}{2krA_m(1 - e^{-1/k})} \right) \quad (47)$$

Although these values are a good guide, again it is more useful to use a error criterion to make the match. This is especially true since the combination of Eq. (42) crossing over to Eq. (43) creates a larger linear range.

2. Results of the comparison for a single adsorption energy - evaluation of s' and b'

One could use two approaches to obtaining s' and b' ; the first of these is to determine the inflection point of Eq. (45) and determine the tangent to this inflection point. The slope and intercept then yields these constants. Table 2 is a listing of some of the constants as a function of r and k . Due to the skewness of the second derivative of this equation, however, the range for a given error is limited. A second approach is to select a permissible error and determine an overall range which meets the requirement. Such a method yields a much broader valid range. With a P_c of -2.5 and an allowed error of 2 %, the range can extend over pressure ranges of a factor of about 10^5 or more. Table 3 contains some examples using this method for the DR isotherm.

In Figs. 1! 4 are some of the $k = 2$ curves, the DR plots, with linear portion predicted from the values from Table 3. The curves generated from the P treatment are plotted in the standard fashion for the DR isotherm. In order to lend some reality to the perspective of these figures, a P_c has been selected in order to plot $\log(P/P_o)^2$ as the x-axis rather than f_1 of Eq. (32). This is not relevant to the discussion since changing P_c merely changes the scale of the axis. In these figures the value for P_c was selected as -2.5. (Note that with the conversions of \ln to \log on **both** axes and this value of P_c that s' needs to be multiplied by 0.0155.) The value for P_c of -2.5 is typical for SiO_2 and other ceramic adsorbents. One of the most noticeable features is the extension of the linearity. This is quite impressive even for the shortest one presented here with $r = 10V_m/A_m$, which is probably into the mesopore range with its complications. This

mesopore adsorption is complicated by the additional concern of the formation of the liquid-gas interface and the pre-filling due to the second application of the Kelvin relationship. This would imply that it would be very difficult to determine from experimental data what the valid range is for this latter case.

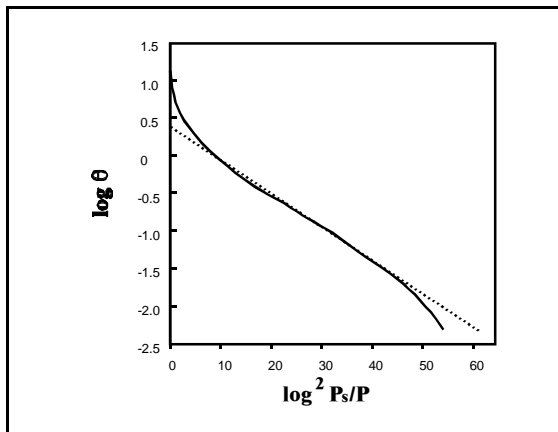


Figure 1 DR plot (solid line) generated from the QM based treatment for $r = 10V_m/A_m$ for a homogeneous (single energy) surface. Dashed line is the linear approximation from table 3.

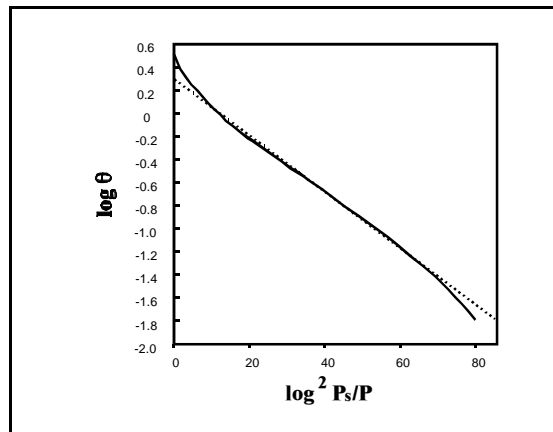


Figure 2 DR plot (solid line) generated from the QM based treatment for $r = 3.3V_m/A_m$ for a homogeneous surface. Dashed line is the linear approximation from table 3.

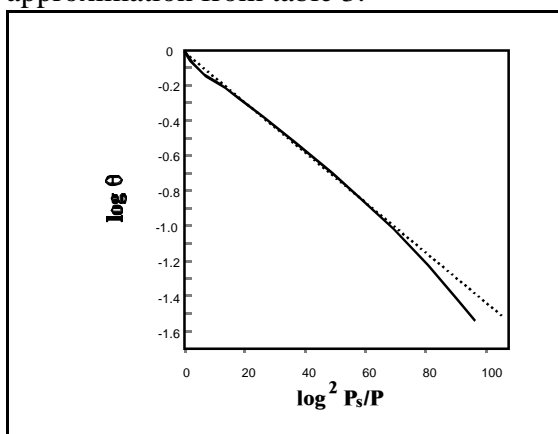


Figure 3 DR plot (solid line) generated from the QM based treatment for $r = 2V_m/A_m$ for a homogeneous surface. Dashed line is the linear approximation from table 3.

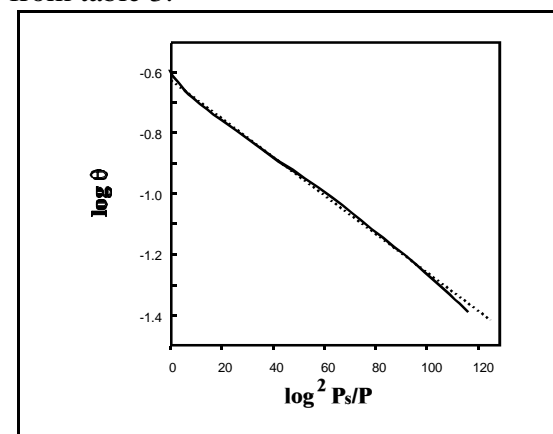


Figure 4 DR plot (solid line) generated from the QM based treatment for $r = 1.1V_m/A_m$ for a homogeneous surface. Dashed line is the linear approximation from table 3.

3. Discussion of Results

The most important result is the large range of validity of the relationship given in Eq. (45). This indicates that the DR and DA equations are indeed justified by the QM/statistical mechanical treatment of adsorption. Furthermore, a similar relationship was found for DRK equation, a point which may be a bit disconcerting to some. (See, for example, the book by Sing and Gregg [34].) One could argue that the valid range does not extend from 0 to 4 and therefore this does not fully validate the DP isotherms. This, however, is much too stringent a requirement, since the actual

applications of these equations usually extend over an even shorter range than demonstrated here. Furthermore, the requirement of one surface energy is also too stringent. In part B, some reasonable distribution of energies is assumed to demonstrate that the range of validity may be extended to effectively meet the more stringent requirement.

The DRK equation states that the intercept of Eq. (16) should be 0. Thus the term $\exp(b)$ is a multiplicative factor which indicates the error in the extrapolations of DRK isotherm. From the intercept values, b , in Table 2, the value obtained by extrapolation to the axis (where $\log(P_o/P) = 0$) should then be between ~0 % and ~20 % too small. This is off-set by the recommended IUPAC correction factor (1.098) for the BET which increases the answer by about 10 % from the liquid density value. It is therefore not surprising that this spread of ± 10 % is typically found when comparisons between materials is determined. (See, for example Granville, Hall and Hope [35].) For the DR/DA equations the intercept of $-\ln(2V_m/rA_m)$ is only slightly different than the numbers presented, especially for the large pore sizes. For smaller pores ($r > 3.3V_m/A_m$), a difference of about 0.01 to 0.02 exists for the intercept, which corresponds to an error of only 2 to 5 %.

Another point to notice from the tables is as follows. At the very low values of θ , lower than a 1 monolayer equivalent, all three equations yield errors greater than 2%. These low coverages, however, are rarely of importance in the application of the DP equations. On the other end of the isotherm, the values of r for which there is the shortest range of validity are for very small pores and the range of measurement is correspondingly short. These theoretical problems are for $r > 2V_m/A_m$ or pores which have a radius less than $2\times$ the molecular diameter. The pore filling is therefore essentially complete before this (then theoretical) problem arises, making the concern irrelevant.

In application of the equations, obtaining the constants s' and b' for any particular sample is relatively simple from the θ equations. This is because the θ equations yields the parameters of pore size, internal surface area (and therefore pore volume), external surface area and surface energy values needed in the calculation. Thus, all the constants can be predetermined in order to calculate the DP parameters. It is, however, very difficult to reverse the process since the energy and pore sizes are bound together with the series expansion constants. Furthermore, the answer is also sensitive to range over which the DP equation is applied. This is similar to the problem of attempting to recover data from the BET parameters without knowing the range of application. A more direct route is to simply simulate the data with the DP equations and refit with the θ plot. This is, unfortunately, still sensitive to the original treatment method, for example the range of the fit.

The mystery as to why the same isotherm can be used to analyze in one case for the pore volume (DR) and in another case for the surface area (DRK) has been mathematically resolved. A further insight into this can be obtained by an inspection of the cross-over criterion for Eq. (42) and Eq. (43). So long as the θ is small enough to satisfy the criterion for Eq. (42) the θ is a modified measure of surface coverage and for $r = 4$, i.e. a flat surface, it will be the coverage. This is more obvious in the approximation the low pressure range given in Eq. (31). The slope of the θ plot (approximately but not quite θ_{obs}) at very low pressures then yields the surface area for pores with radii equal to or greater than the adsorbate molecule radius. The θ_{obs} plot will then deviate downward with increasing pressure due to the geometrical constraints. From the geometrical constraints a value for r can be obtained in order to calculate θ from θ_{obs} . For values of θ greater than the criterion of Eq. (43), the

intercept for $\ln(2)$ will yield a 2 value of $rA_m/2V_m$, from which the pore volume may be calculated. More simply put in terms of pore volume, this should then be:

$$V_{pore} = V_m e^{b'} \quad (48)$$

A characteristic of the larger micropores is that the DR and DA plots have a substantial deviation at high pressures. This deviation would become even more obvious as one were to reach the mesopore range except that the capillary filling phenomenon obscures this. For such curves, the actual intercept, not the extrapolated one from the linear portion of the curve, should yield the proper value of the pore volume. In the cases of very little external surface area, this extrapolation is better performed on the untransformed isotherm, that is the plot of amount adsorbed versus pressure. In the rare case where the external surface area on a porous material is significant, such an extrapolation may be impossible and one needs to use the P representation to sort out the physical quantities.

Notice that the last term of Eq. (45) is fairly small or negative for small pore sizes. The actual curve will bend upward to 0 when the value is negative, thus giving the correct answer for the pore volume in the original data. This is to be expected since the intercept at high pressures should be the \log_{10} of the pore volume, in this equation given in terms of 2 . The scaling of the pressures with the energy term is also exactly what happens in the DR and DA equations with the energy terms. Given that Eq. (41) was used to derive this relationship, it is also not surprising that upon inspection of the generated DA plots this relationship holds up very well above a pore radius greater than $1 \times$ the value for V_m/A_m . At a value of $0.5 \times$, which is the smallest cylindrical pore which can be measured, the relationship is off by about 5%. These points are more obvious by inspection of Figs. 3 and 4. (Fig. 4 is for $r = 1.1 V_m/A_m$ in place of $r = V_m/A_m$ to avoid convergence problems.)

A discussion of the advantages and disadvantages of the two different representations of the isotherms for porous materials is in order. The primary advantage of the Dubinin-Polanyi formulation is the ease of analysis. Adding parameters beyond the DA representation does not seem to be justified without some prior knowledge about energy distributions. The reason for this is that the adsorption data are usually not obtained over a large enough range to justify adding any additional parameters. The primary disadvantage of the DP representation is that it does not always yield an answer for the pore sizes, especially if the experimental, untransformed, intercept and the DA-plot extrapolated intercept are not the same. It definitely has the disadvantage that the external surface area cannot be accounted for and can therefore yield a large error if it is present to a significant amount. This is not usually the case for very microporous material, such as zeolites, where the external surface area is less than 1%. The primary disadvantage of the P representation is the difficulty of the calculation. A single pore-sized material is not too difficult to set up in a spread sheet, but accounting for multiple pore sizes appears to be a very difficult computation task. The advantage of such a method is that it will yield the adsorption energy, the pore radius, the pore volume and the external surface area. As demonstrated in part B, An adsorption energy distribution is also not difficult to set up but determining the energy distribution itself can be problematic.

Both methods have difficulties with mesoporosity. For the P theory, however, this is a small addition to the spread sheet which is used. Unfortunately, the actual forms of the equations that need to be added onto the P plot is uncertain. No provisions or claims have been made for the Dubinin formulations, but it might be possible to use the basic plot to unscramble the mesoporosity.

Conclusions

The (DP) isotherms may easily be justified upon the basis of a simple QM description of adsorption. Incorporation of the QM effects eliminates the traditional criticism of the DP isotherms presented by Avgul, et. al. [36]. The ones investigated in this report are the DR the DA and the DRK isotherms. It would seem reasonable that other more complicated forms would also fit within the framework of the derivations. The range of validity vis-a-vis the QM based isotherm derivation, given the designation as the P description, is very large. With only a single energy of adsorption, i.e. a perfectly homogeneous surface, the QM derived energy spread in the P equation is enough using the inflection point technique to validate the DP isotherm within 2 % over a range in pressure of at least a factor of 100 depending upon pore size. Furthermore, the valid range is precisely that for which these equations are used the most. (The match between the two formulations should be much better than derived by this technique, as illustrated for the matches made with the DR equation using only the 2 % range criterion. In that case the range of validity in pressure was at least a factor of 400.) Such a match would seem to validate both the DP description, in that it is also based in a QM/statistical mechanical derivation, and the P description, in that it is now strongly supported by extensive experimental data.

Acknowledgments

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Appendix A. Nomenclature

$\$$	= Adsorbate dependent parameter in the Dubinin-Polanyi equations
$\left\{ \right.$	= surface tension, J/m ²
$\left\{ \right._a$	= surface tension of adsorbent, J/m ²
$\left\{ \right._4$	= surface tension as pressure goes to P_o , J/m ²
$\left\{ \right._*$	= Kronecker delta function
$\left. \right) P$	/ $P \neq P_c$
ϵ	= energy of interaction between adsorbed molecules, J/mol
ϵ_t	= translation energy, J/mol
2	= equivalent monolayer coverage = moles of adsorbate divided by the number of moles that calculate to cover the surface by exactly a single layer, mol/m ²
2_1	= coverage of the surface by the 1st adsorbed layer
F	= 1 standard deviation
P	= the chi function defined in Eq. (4)
P_c	= the critical chi value defined by Eq. (5)
Q	= wave function
a	= area of an adsorbed molecule, m ²
A	= Dubinin's adsorption potential, J/mol
A_m	= molar area of adsorbate = $N_A \times a$, m ² /mol
A_s	= surface area or, in the QM derivation, the area of an adsorbent patch, m ²
b	= intercept of a line
B	= the energy term in the Dubinin-Polanyi equations
b'	= another defined intercept of a line
c	= starting position of the adsorbate "tooth", m
d	= ending position of the adsorbate "tooth", m

- E = total energy in WKB approximation, J
 E_a = energy of adsorption as define by Fuller which = $V_{ad} - \epsilon$, J/mol
 E_f = energy after perturbation (finish), J
 E_i = energy of adsorption for the nth molecule (i is an index), J/mol
 E_s = non-perturbed energy (start), J
 f_1 = function defined by Eq.(9)
 f'_1 = function defined by Eq.(32)
 f_2 = function defined by Eq.(9)
 f'_2 = function defined by Eq.(42)
 $g(x)$ = g function in WKB approximation
 h = Plank's constant
 $h(x)$ = h function in WKB approximation
 i = index for the ith molecule
 j = index for the jth molecule
 k = the exponential constant in the Dubinin-Polanyi equations. For DR $k = 2$.
 k = Boltzmann constant
 l = box length for the particle in the box
 m = mass of a particle
 n_A = the number of moles of adsorbate
 N_A = Avogadro's number
 n_{Ao} = the number of moles to completely fill the pores of the adsorbent, mol
 n_b = number of moles at the intercept of the DRK equation, mol
 n_m = the monolayer equivalent moles adsorbed, mol
 n_x = quantum number (translational)
 P = pressure, Pa
 P_o = vapor pressure of an adsorbative over a curved surface = the modified vapor pressure in the Kelvin equation, Pa
 P_s = vapor pressure over a liquid with a flat surface, Pa
 Q = constant defined by Eq. (10)
 R = the gas constant
 r = adsorbate-adsorbent radius of curvature . pore radius (cylindrical), m
 r_F = the Freundlich isotherm constant
 s = (not a subscript) slope of a line
 s' = another defined slope of a line
 $S(x)$ = S function in WKB approximation
 t = average thickness of the adsorbed layer, m
 T = temperature /K
 $U() P)$
 $U() P)$ = the unit step function at $P = P_c$
 V = volume of the adsorbate, m^3
 $V(x)$ = potential energy function in WKB approximation, J
 V_{ad} = energy of adsorption not including ϵ , J/mol
 V_m = molar volume of adsorbate, m^3/mol
 W = W values in WKB approximation
 x = in the WKB approximation - distance, m, otherwise a dummy argument.
 z = the ratio a/A_s (in QM derivation)

Appendix B. Use of the WKB approximation to derive the P equation.

The WKB (Wentzel-Brillouin-Kramers, see for example Jeffreys[37] or Smith's book on Wave Mechanics of Crystalline Solids[38]) approximation is used to derive the P isotherm by the following. For a particle in a (1D, 2D is obviously similar) potential box, for a particular quantum number, n_x , the wave function, Q , is of the form:

$$\frac{\partial^2 \Psi}{\partial x^2} - g^2(x) \Psi = 0 \quad (49)$$

where:

$$g^2(x) = \frac{8m\pi |V(x) - E|}{h^2} \quad (50)$$

The solution for \mathbf{R} is then:

$$\Psi = W h(x) e^{S(x)} \quad (51)$$

where

$$S(x) = \pm \int^x g(x) dx \quad (52)$$

and

$$h(x) = W [g(x)]^{1/2} \quad (53)$$

A comparison is then made between a particle in the empty box and a particle in a box with a single "tooth" as a slight perturbation. In order to have \mathbf{R} fulfill the boundary conditions at the edge of the box (regardless of what those are) the function $V(x) - E$ for the perturbed system needs to be adjusted so that $S(x)$ at both ends will match the original function for the empty box. Assuming a non-perturbed E of E_s (for starting,) this E must be adjusted to another value, E_f (for finishing.) Using a box size of l and a tooth located between $x = c$ and d , where $d - c \ll l$ then Eqs. (50), (51) and (53) require:

$$\sqrt{E_s} l = \sqrt{E_f - V} (d - c) + \sqrt{E_f} (l + c - d) \quad (54)$$

Factoring out E_f :

$$\sqrt{E_s} l = \sqrt{E_f} \left[l + c - d + (d - c) \sqrt{1 - \frac{V}{E_f}} \right] \quad (55)$$

Expanding the last square root and, since $V \ll E_f^3$, cutting off the higher term and regrouping:

$$\sqrt{E_s} l = \sqrt{E_f} \left[l - (d - c) \frac{V}{2E_f} \right] \quad (56)$$

Defining a quantity, z : (In the two dimensional box, this corresponds to the ratio of a/A_s , where a is the area of an adsorbate molecule and A_s is the area of the adsorbent patch or the surface area.)

$$z = \frac{d - c}{l} \ll 1 \quad (57)$$

³ The assumption $V \ll E_f$ is not totally necessary. If this were not the case then the expansion would need to be carried out further, in which case a new value of V would be obtained in the subsequent derivation differing from the V given at the beginning. The final form of ?, however, would remain unchanged.

dividing through by l and then squaring both sides:

$$E_s = E_f \left(1 - \frac{V}{E_f} z + \left(\frac{V}{2E_f} \right)^2 z^2 \right) \quad (58)$$

The last term is very small since it contains z^2 , and one gets:

$$E_f = E_s + Vz \quad (59)$$

Notice that the depth of the box potential well does not affect the results, since the original condition was that the final wave function matches the original wave function both in slope and magnitude at the boundaries $x = 0$ and $x = 1$. Therefore, the original potential box could be a box of potential depth V_{ad} and the tooth would have a depth (from the top of the well) of ϵ . Thus Eq. (59) becomes:

$$E_f = E_s + (V_{ad} - \epsilon)z \quad (60)$$

The same answer would be obtained for E_f if the particle were in an unperturbed box of potential V_f of:

$$V_f = V_{ad} - (V_{ad} - \epsilon)z \quad (61)$$

or rearranging:

$$V_f = (V_{ad} - \epsilon)(1 - z) + \epsilon \quad (62)$$

This can be extended to subsequently added "teeth," with the general results for the i th tooth, the energy, E_i , is related to the previous E , E_{i-1} , by Eq. (59). Repetition of the above steps leads to the answer that for the j th molecule the V_f is related to the V_{ad} (see the next section for proof) by:

$$V_{f,j} = (V_{ad} - \epsilon)(1 - z)^{j-1} + \epsilon \quad (63)$$

where the subscript j indicates this is for the j th molecule. The expansion is only for the interaction to the surface and does not take into account the interaction of the j th molecule with the previous $(j - 1)$ molecules. Thus, $(j - 1)\epsilon$ must be added to obtain the total interaction for the adsorption of the j th molecule. Assuming a reasonably large number of adsorbed molecules, i , and using the definition that $z = ia/A_s$:

$$V_{f,i} \approx E_a \left(1 - \frac{\theta}{i} \right)^i + i\epsilon \quad (64)$$

Eq. (64) is the starting point for deriving the grand canonical partition function in the usual fashion.

B.1. proof of Eq. (63)

Eq. (62) is the starting point for proving Eq. (63) by the usual recursion technique. Designate V_i as the V_f for the i th molecule. Then Eq. (62) is

$$V_2 = (V_{ad} - \epsilon)(1 - z) + \epsilon \quad (65)$$

then:

$$V_3 = (V_1 - \epsilon)(1 - z) + \epsilon \quad (66)$$

thus:

$$V_3 = \left(\left\{ \left[V_{ad} - \epsilon \right] [1 - z] + \epsilon \right\} - \epsilon \right) (1 - z) + \epsilon \quad (67)$$

or:

$$V_3 = (V_{ad} - \epsilon)(1 - z)^2 + \epsilon \quad (68)$$

But if:

$$V_i = (V_{ad} - \epsilon)(1 - z)^{i-1} + \epsilon \quad (69)$$

and since:

$$V_{i+1} = (V_i - \epsilon)(1 - z) + \epsilon \quad (70)$$

then:

$$V_{i+1} = \left(\left\{ (V_{ad} - \epsilon)(1 - z)^{i-1} + \epsilon \right\} - \epsilon \right) (1 - z) + \epsilon \quad (71)$$

or:

$$V_{i+1} = (V_{ad} - \epsilon)(1 - z)^i + \epsilon \quad (72)$$

substituting $j = i + 1$ yields Eq. (63). QED.

Appendix C - Derivation of spreading pressure from P

The energy of adsorption for a curved surface will differ from that of a flat surface. One way of explaining from a macroscopic, i.e. thermodynamic, point of view is to assume that the Kelvin equation applies to the curved surface, changing the activity of the adsorbate in relation to the adsorbative. From this point of view, in order to calculate this effect one needs the spreading pressure relationship which is derived from the isotherm equation. One can arrive at two different expressions for spreading potential from the P theory depending upon the reference (. Starting with the appropriate Gibbs-Duhem equation for adsorption on the solid surface:

$$d\gamma = -\frac{RTn_A}{A_s} d \ln \left(\frac{P}{P_o} \right) \quad (73)$$

Here A_s is the surface area. P_o is the saturation vapor pressure over a surface of the same curvature. From Eq. (7) for $P > 0$:

$$\frac{n_A}{A_s} = \frac{\theta}{A_m} = -\frac{1}{A_m} \ln \left(\frac{A}{E_a} \right) \quad (74)$$

where A_m is the molar area. In P theory this molar area is derived from the liquid density without any correction factor or:

$$A_m = (V_m)^{\frac{2}{3}} (N_A)^{\frac{1}{3}} \quad (75)$$

Where V_m is the molar volume and N_A is Avogadro's number. Eqs. (73) and (74) yield:

$$d\gamma_a = -\frac{1}{A_m} \ln\left(\frac{A}{E_a}\right) dA \quad (76)$$

Using the normal γ_o , i.e. the bare surface value in which case an integration from $P = 0$ to P is performed, the equation is:

$$\gamma_a - \gamma_o = -\frac{1}{A_m} \left[\ln\left(\frac{A}{E_a}\right) - 1 \right] A + \frac{E_a}{A_m} \quad (77)$$

An alternative and more useful expression for γ_a may be obtained by reference to γ_a , the value for this in the bulk liquid. One can integrate from P to P_o instead, with γ_a going from γ_a to γ_a , to obtain:

$$\gamma_a - \gamma_\infty = -\frac{1}{A_m} \left[\ln\left(\frac{A}{E_a}\right) - 1 \right] A \quad (78)$$

This equation looks simpler when rewritten as:

$$\gamma_a - \gamma_\infty = -\frac{(\Delta\chi + 1)}{A_m} \ln\left(\frac{P}{P_o}\right) \quad (79)$$

It is better at this point to express this relationship in terms of P and not in terms of γ_a . The reason for the caveat is that γ_a can be modified by geometrical considerations exclusive of surface tension effects. On the other hand, P is not altered merely by geometrical constraints.

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Table 1

Adsorbate density variations and analysis of radius from the density relationship in the P equations.

Molar volumes, V_m , of Ar adsorbed in confined pores compared to the bulk liquid density (according to Dubinin, Zhukovskaya and Murdmaa[15]) and the calculated pore size from P theory density.

Adsorbent	V_m /mL mol ⁻¹	D_{ad}/D_{liq}	coverage at pore filling /monlayers	pore size /nm
CaA zeolite	32.4	0.841	1.84	0.80
NaX zeolite	31.4	0.869	2.03	0.85
AU-1 carbon	33.9	0.805	1.63	0.74
AU-2 carbon	31.2	0.875	2.09	0.87
bulk liquid	27.3			

Table 2

Calculations of the constants s' and b' as a function of k and r .

	$k=2$	$k=3$	$k=4$		$k=2$	$k=3$	$k=4$
$r = 4$				$r = 5.0V_m/A_m$			
$)P_i = 0.5000$	0.5000	0.3333	0.2500	$)P_i = 0.632$	0.411	0.306	
$s' = 2.718$	2.718	-2.718	-2.718	$s' = -1.792$	-1.523	-1.280	
$b' = 0.307$	0.307	0.099	-0.386	$b' = 0.287$	0.084	-0.355	
$r = 100.V_m/A_m$				$r = 3.3V_m/A_m$			
$)P_i = 0.509$	0.509	0.337	0.253	$)P_i = 0.718$	0.459	0.337	
$s' = -2.660$	-2.660	-2.636	-2.610	$s' = -1.455$	-1.164	-0.911	
$b' = 0.309$	0.309	0.096	-0.383	$b' = 0.228$	0.113	-0.370	
$r = 20.V_m/A_m$				$r = 2.5V_m/A_m$			
$)P_i = 0.530$	0.530	0.352	0.263	$)P_i = 0.849$	0.510	0.371	
$s' = -2.444$	-2.444	-2.335	-2.227	$s' = -1.168$	-0.896	-0.659	
$b' = 0.312$	0.312	0.079	-0.360	$b' = 0.131$	0.167	-0.406	
$r = 10.0V_m/A_m$				$r = 2.0V_m/A_m$			
$)P_i = 0.562$	0.562	0.371	0.278	$)P_i = 1.594$	0.580	0.410	
$s' = -2.201$	-2.201	-2.017	-1.840	$s' = -0.748$	-0.690	-0.482	
$b' = 0.312$	0.312	0.079	-0.360	$b' = -0.064$	-0.250	-0.465	

Table 3

Some values for s' and b' for the DR isotherm and the range of application for an allowed 2 % error

	$r = 100V_m/A_m$	$r = 5.0V_m/A_m$	$r = 2.0V_m/A_m$
) P range	0.20 6 1.12	0.25 6 1.42	0.51 6 6.5
s'	-2.880	-1.934	-0.915
b'	0.389	0.359	-0.020
P_{max}/P_{min}	4.2×10^2	1.8×10^3	3.5×10^5
	$r = 20.0V_m/A_m$	$r = 3.3V_m/A_m$	$r = 1.7V_m/A_m$
) P range	0.21 6 1.15	0.29 6 1.66	0.63 6 3.6
s'	-2.632	-1.569	-0.653
b'	0.390	0.290	-0.226
P_{max}/P_{min}	5.0×10^2	4.8×10^3	1.1×10^5
	$r = 10.0V_m/A_m$	$r = 2.5V_m/A_m$	$r = 1.1V_m/A_m$
) P range	0.22 6 1.25	0.30 6 100+	0.67 6 3.5
s'	-2.378	-1.306	-0.407
b'	0.390	0.214	-0.622
P_{max}/P_{min}	8.1×10^2	9.1×10^5	9.3×10^5