Equivalency of the Dubinin-Polanyi Equations and the QM Based Sorption Isotherm Equation. - Part B Simulations of Heterogeneous Surfaces

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Abstract:

In Part A it was 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. Assuming no other energy distributions than that obtained in the QM treatment, the DR , DA and DRK equations were found to be valid within a specified error and pressure range. In this part, heterogeneous adsorption will be simulated to demonstrate the possibility of a wider range of validity, especially in the very low pressure ranges. With a logarithm-normal adsorption energy distribution of $F = 0.25$ (corresponding to about 2 kJ mol^{-1} for liquid N_2 adsorption on ceramics) the range of validity in coverage increases to an amazing factor of about 10^{10}. Such a distribution also reveals the low pressure equivalence of the Freundlich isotherm, the QM and the DP formulations.

Key words:
Adsorption, Porosity measurements, Physical adsorption, Isotherms, Physisorption

1. Introduction:
A short review of the Dubinin-Astakhov (DA) and the quantum mechanical derived isotherm equations were given in the preceding paper (part A). The generalized form of the DA equation is:

$$\ln\left(\frac{n_A}{n_{Ao}} \right) = B\left(\frac{T}{\beta} \right)^k \ln^k\left(\frac{P_s}{P} \right) \tag{1}$$

Where P is the pressure and P_s is the vapor pressure over a flat liquid surface. B and $\$$ are constants.

The Quantum Mechanical (QM) derivation referred to as the chi theory equation is written as:

$$\frac{n_A}{n_m} = \left(\chi - \chi_c \right) U\left(\chi - \chi_c \right) \tag{2}$$

where P and P_c are defined by:

$$\chi \equiv -\ln\left[\ln\left(\frac{P_o}{P} \right) \right] \quad \text{and} \quad \chi_c \equiv -\ln\left(\frac{E_a}{RT} \right) \tag{3}$$

The function U is the unit step function and P_o is vapor pressure over the adsorbate which could be different than P_s for curved surfaces. As pointed out in part A, this difference needs to be accounted for when calculating adsorption in pores. Defining

) $P = P - P_c$ and using the symbol 2 for n/n_m a the very simple representation of the chi theory is:

$$\theta = \Delta\chi\,U(\Delta\chi) \tag{4}$$

In part A the chi and DR equations were demonstrated to be mathematically identical over a large pressure range. The range of validity corresponded to those pressures where the DA equation was used the most for measuring porosity. To do this, only one E_a was assumed which is that of a homogeneous surface. There are some cases for which a deliberate effort has been made to obtain a surface that had one adsorption energy. For example, Gammage, et. al. [1], used special treatments of thoria to accomplish this. These cases are, however, unusual. The possibility of two or more energies of adsorption, or even a distribution of energies, is more likely. In this part, Eq. (4) will be modified to account for a logical distributions of energies.

2. Methodology for simulating the Isotherms

One can modify Eq. (4) to take into account a distribution in the adsorption energy, E_a. The modification would take into account the possibility of several patches (i.e. "boxes") which differ in E_a. Differentiating one obtains:

$$\frac{d\theta}{d\chi} = U(\Delta\chi) \tag{5}$$

Differentiating again:

$$\frac{d^2\theta}{d\chi^2} = \delta(\Delta\chi) \tag{6}$$

where * is the Kronecker delta function. This equation indicates that, other than the energy spread due to the QM treatment, there is one and only one adsorption energy, i.e. there is only one energy for the first adsorbate particle regardless of where on the surface it adsorbs. Even a close approximation of such a perfectly homogeneous surface is a rare exception. One may break this assumption by replacing the single delta function with several delta functions or with some reasonable distribution (differential) function such as the normal distribution. Use of the normal distribution in P_c would imply a logarithm-normal distribution in energy as described by Sing and Gregg [2] which is a reasonable distribution for modeling. This logarithm-normal distribution has the advantage that only negative energies are used going from the liquid state to the adsorbed condition. The adsorption is thus exothermic from the liquid state to the adsorbed state or by the convention previously stated, $E_a > 0$. The replacement for Eq. (6) would then be:

$$\frac{d^2\theta}{d\chi^2} = \frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{(\chi - \langle\chi_c\rangle)^2}{2\sigma^2}} \tag{7}$$

Double integration of Eq. (7) yields a function corresponding to Eq. (4) for the more realistic case of a spread of surface energies. Eq. (7) will be used for the energy distributions in some simulations. These simulations are intended to illustrate that, given some reasonable assumptions about the nature of the surface energies, the DA equations might extend over an extremely wide range.

In part A, equations were derived that took into account the surface curvature and the restriction in geometry encountered with cylindrical pores. These corrections are important in both the high and low pressure regions. However, in the low pressure range a simplified correction can be used:

$$\Delta \chi_{obs} = \frac{\Delta \chi}{1 + V_m/rA_m} \tag{8}$$

where r is the radius of the cylindrical pore and V_m and A_m are the molar volume and area of the adsorbative in the liquid phase. ΔP_{obs} is an experimentally observable quantity similar to ΔP defined by using P_s in place of P_o in Eq. **(3)**.

3. Calculations Using a Distribution of Adsorption Energies.

What distribution should be used is quite questionable and depends upon the details of the surface. Eq. **(6)** could be used as the basis to construct any arbitrary distribution. For illustration, a logarithm-normal distribution of the energy, as mentioned previously as Eq. **(7)**, will be used in some typical calculations. It turns out that the choice of the distribution is only important in the low pressure region of the isotherm. For the high pressures the isotherms are minimally sensitive to the choice of the distribution used. This was referred to in the original presentation of the theory as the threshold phenomenon [3]. In practical terms, the value of pressure above which the distribution problem may be ignored is from 1 x 10^{16} P_s for high energy material, such as ceramics, to about 1 x 10^{-3} P_s for very low energy materials such as perfluoropolyethylene.

Eq. **(7)** is the expression of the postulated logarithm-normal distribution in energy. For the low pressure region only $<P_c>$, r and F need be selected. With a large r, a double integration of this equation. , yielding the integral of the area function in terms of P, will yield the low pressure isotherm. In the low pressure range, given a reasonable value of r the difference between ΔP_{obs} and ΔP is a multiplicative factor as indicated in Eq. **(8)**. Thus, even with a reasonable value of r associated with micropores, the functionality of Eq. **(7)** may be used with the proviso that the $<\Delta P_{obs}>$ is that give by Eq. **(8)**.

This simple method does not account for the geometrical restraints of the pores which become important at the higher pressures. The simulation of the full isotherm is accomplished by selecting multiple theoretical P and P_c values according to Eq. **(7)** and using the equations

$$\chi_c = \chi_{c,obs} + \ln\left(1 + \frac{V_m}{rA_m}\right) \tag{9}$$

and

$$\chi = \chi_{obs} + \ln\left(1 + \frac{V_m(\Delta \chi + 1)}{rA_m}\right) \tag{10}$$

several times to generate P_{obs} and $P_{c,obs}$. (Alternatively, the function f' in part A may be used in order to yield a simulation independent of the selection P_c.) The corrections for the geometrical restrictions are then applied to ΔP in the same fashion as for the homogeneous surface. The multiple P_{obs} plots are then added.

4. Low Pressure Results and the Selection of a σ

The first question is: "What is the appropriate standard deviation, σ, to use in P_c to match the various DA isotherms?" This can be answered with the simple double integration of Eq. **(7)** since only the low pressure region need be considered. The results indicate the σ is dependent upon k. Appendix B presents some approximations that may be used. For the DR equation, for which $k = 2$, $\sigma = 0.25$. Fig. 1 is an illustration of the match in the low pressure region for the DR isotherm. An interesting side-bar is that at a $\sigma = 0.50$, the Freundlich isotherm is exactly matched in the low pressure region. This is illustrated in Fig. **2**. The Freundlich isotherm constant, r_F, in the equation:

$$\theta = KP^{1/r_F} \tag{11}$$

is related to E_a by (see appendix B):

$$r_F = \exp\left(\frac{E_a}{RT} - 1 \right) \tag{12}$$

The value of r_F has no effect the value of σ, but merely shifts the center point of the adsorption energies according to Eq. **(12)**. Thus the Freundlich isotherm is just another case of the DP sets of isotherms with $k . 1$, at least in the low pressure range. Notice also that "Henry's law," or when $r_F . 1$, is therefore also a special case of the Freundlich isotherm when $E_a . RT$.

5. High Pressure Results using the DR σ

Of greater interest is how well a logarithm-normal distribution matches experimental results into the higher pressure range. For this the full accounting of porosity must be simulated as described above. To illustrate the effect of this distribution simulations for several values of the pore size parameters were performed. For these simulations the DR distribution, $\sigma = 0.25$, was used. Repeated use of the equation from part A which takes into account the effects of curvature (Eqs. **(9)** and **(10)**) and geometrical restriction (Eqs. (43) and (44) of part A) were performed and added according to this distribution. The value of σ selected corresponds to about 25 % in energy. For a typical ceramic material and liquid nitrogen adsorption this implies $\sigma . 2$ kJ mol^{-1}. The plots for values of r of ∞ (flat surface,) $10\times$, $4\times$ and $2\times V_m/A_m$ are presented in Fig, **3**. The range of validity is greatly expanded over that for a single adsorption energy as presented in part A. Notice that the $\log^2(P)$ is over a span of roughly 115 in this figure, corresponding to a pressure range of a factor of about 5×10^{10}. In part A the valid pressure range varied from a factor of 100 to 10^5 depending upon the sample and methodology of determining the slope and intercept. Here the linearity begins to break down for such a large range of pressures with $r = 2$ as illustrated by the dashed line.
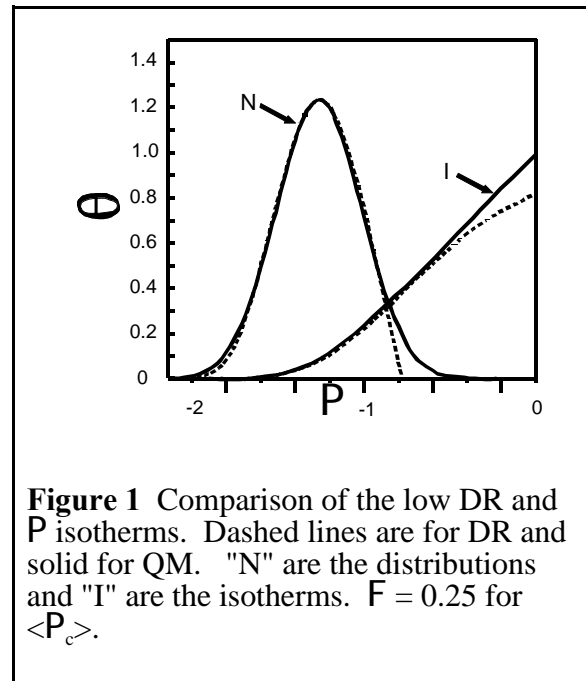

Figure 1 Comparison of the low DR and ϕ isotherms. Dashed lines are for DR and solid for QM. "N" are the distributions and "I" are the isotherms. $\sigma = 0.25$ for $\langle P_c \rangle$.

In Fig. **3** the DA parameter, and thus F, is held constant ($k = 2.00$) and the pore size, r, is varied. Similar calculations may be made holding r constant and varying F to yield the relationship between F and k. Fig. **4** gives the results of several calculations with $r = 4V_m/A_m$. The DR equation, $k = 2$, is shown to be at $F \doteq 0.25$ and the Freundlich isotherm, $k = 1$, at $F \doteq 0.50$ as expected.

6. Discussion of Results

In part A the identity of the Dubinin-Polanyi and the chi theory representations of the isotherm were demonstrated over a pressure range that covers most of the reported literature data. One could argue that the homogeneous surface assumed in part A is unrealistic, thus invalidating the derivation. In this part, it is demonstrated the imposition of the heterogeneous surface assumption and an energy distribution could lead to an even broader range of validity.

Figure 2 Comparison of the Freundlich isotherm (dashed lines) with the P generated isotherm with a distribution of $F = 0.50$ for $<P_c>$ (solid lines) demonstrating it is a special case of the DP isotherm.

If one were to use the above equations and impose upon the energy a distribution as specified by Eq. **(7)** the DR plot becomes linear over an astoundingly large range in adsorption. With the use of a standard deviation corresponding to about a 25 % change in energy, the fit to the DR equation is linear within 2 % over a range of adsorbed amount of greater than a factor of 1×10^{10}! Fig. **3** illustrates four examples of such a comparison of the P equation to the DR formulation. Normally, observations for amount adsorbed is over a span of values that is a factor of about 10 and occasionally 100. Such a large range is rarely recorded. One exception is by Hobson [4] who measured the adsorption of Ar, Kr and Xe on porous silver, a material that one would expect to be very heterogeneous. The linearity for adsorption of Ar was over a range in adsorbate volume adsorbed of about 10^3.

Figure 3 DR (DRK, $r = 4$) P generated isotherms with a log normal distribution of adsorption energies for various values of r (pore radius.) $F = 0.25$ in $<P_c>$.

Unfortunately, with the inclusion of an energy distribution, the values for the slope and intercept for the DP plot change from that given in part A. To calculate these, the energy distribution on the surface is required. Thus the importance of the low pressure data, if one uses the DR formulation, becomes critical.
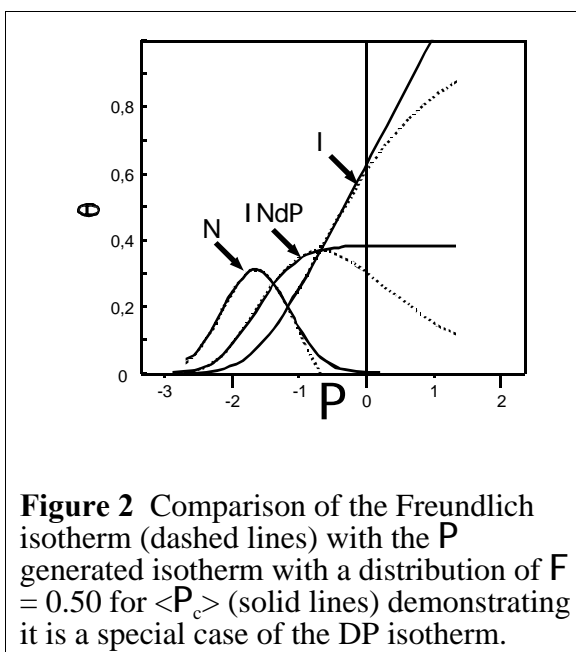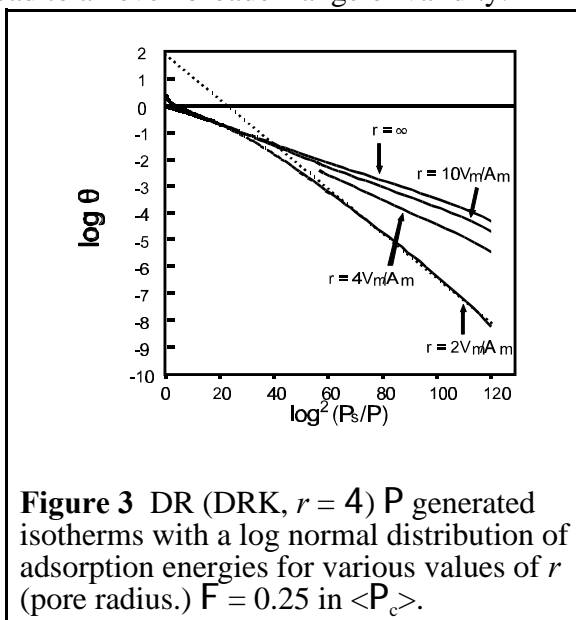
7. Conclusions

In part A the range of validity of the DP isotherm for homogeneous surfaces in comparison to the chi theory is very large. Even though the range of validity is that for most experimentation, the question remained as to what effect a heterogeneous surface would have. This is most critical in the low pressure region (practically speaking below about 10^{-4} atm.) for which the DP and Freundlich (Henry's law being a special case of Freundlich) isotherms are good descriptions. With an assumed logarithm-normal distribution in adsorption energy with a spread of only 25 %, the range of validity extends into the this very low pressure range. With this degree of energy distribution the range of validity extends over a range of about 10^{10} in coverage and a factor greater than of 10^{10} in pressure. Given this information, the conclusion of part A holds up, i.e. that both the DP description and P description are validated, The DP description is strongly supported on theoretical grounds and the chi theory is strongly supported by extensive experimental data gathered and analyzed using the DP description.
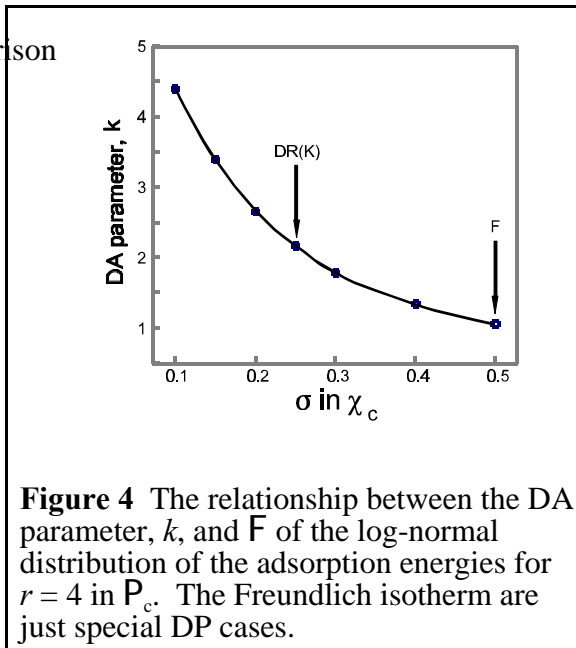
Figure 4 The relationship between the DA parameter, *k*, and F of the log-normal distribution of the adsorption energies for $r = 4$ in P_c. The Freundlich isotherm are just special DP cases.

Acknowledgements

Appendix A - Nomenclature - List of symbols

$\$$ = a constant in the Dubinin-Polanyi equations that depends upon the adsorbent.
$*$ = Kronecker delta function
$)\mathsf{P}$ $/\mathsf{P} ! \mathsf{P}_c$
$,$ = energy of interaction between adsorbed molecules, J/mol
2 = equivalent monolayer coverage = moles of adsorbent divided by the number of moles that calculate to cover the surface by exactly a single layer, mol/m^2
F = 1 standard deviation
P = the chi function defined in eq.**(3)**
P_c = the critical chi valued defined by eq.**(3)**
P_{obs} = the observed chi function referenced to P_s defined in eq.**(10)**
$\mathsf{P}_{c,obs}$ = the observed critical chi function referenced to P_s defined in eq.**(9)**
A_m = molar area of adsorbent = $N_A \times a$, m^2/mol
B = the energy term in the Dubinin-Polanyi equations
b' = defined intercept of a line connecting the DP and chi descriptions
c = lumping of several constants (energy, temperature, etc.) in the chi equation.

E_a = energy of adsorption (defined as positive)
k = the exponential constant in the Dubinin-Polanyi equations. For DR $k = 2$.
n_A = the number of moles of adsorbent
n_m = the monolayer equivalent moles adsorbed, mol
P = pressure of the adsorbative, 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
R = the gas constant
r_F = the Freundlich isotherm constant
s' = defined slope of a line connecting the DP and chi descriptions
T = temperature /K
$U() P)$
= the unit step function at $P = P_\varsigma$
V_m = molar volume of adsorbent, m^3/mol

Appendix B - Approximations to equate energy distributions of the DP with P

Using the generalized form of the DP equation:

$$\theta = e^{A \ln^k(P_o/P)} \tag{13}$$

and defining $1/r_F$ as:

$$\frac{1}{r_F} = -A e^{+k\chi_c} \tag{14}$$

The P representation of the generalized DP equation (for low pressures) is obtained as:

$$\theta = e^{-ce^{-k\chi}} \tag{15}$$

where c includes several constants (see part A.) To obtain the energy distribution, this is differentiated twice to yield:

$$\frac{d^2\theta}{d\chi^2} = k^2\left(c^2 e^{-2k\chi} - ce^{-k\chi}\right)e^{-ce^{-k\chi}} \tag{16}$$

This distribution should then match the distribution given in Eq. (7). To find the maximum value for Eq. (16), the third derivative is set to zero and the appropriate root selected. Matching this to $<P_c>$ Eq. (7) yields:

$$<\chi_c> = -\frac{0.96242365\ldots + \ln(r_F)}{k} \tag{17}$$

since:

$$-\ln\left(\frac{3 - \sqrt{5}}{2}\right) = 0.96242365\ldots \approx 1 \tag{18}$$

and the curvatures match at the max when:

$$\sigma = \frac{0.96242365\ldots}{2k} \tag{19}$$

Eq. **(12)** is the approximation from Eq. **(17)**; whereas, the standard deviations of the chi equation for the various forms of the DP equations may be obtained from Eq. **(19)**. Fig. **4** yields slightly different answers for some of the DP cases. This figure was generated from the full isotherm simulations and not simply from the low pressure considerations.

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