Direct Multilayer Adsorption of Vapor in Solids with Multiscale Porosity and Hindered Adsorbed Layers in Nanopores

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Direct Multilayer Adsorption of Vapor in Solids with Multiscale Porosity and Hindered Adsorbed Layers in Nanopores

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**Abstract:** Hindered adsorbed layers completely filling the nanopores must cause significant deviations from the classical BET isotherms for multimolecular adsorption of vapor in porous solids. Since the point of transition from free to hindered adsorption moves into wider nanopores adsorption layer exposed to vapor gets reduced by an area reduction factor that decreases with increasing adsorbed volume, and thus also with increasing vapor pressure (or humidity). The area reduction factor does not affect the rates of direct adsorption or condensation from individual vapor/gas molecule, which represent a local process, but imposes a lateral constraint on the total area and volume of the free portion of the adsorption layer that is in direct contact with vapor. Assuming an inverse power law for the dependence of the area reduction factor on the number of molecular layers, one can express the modified isotherm in terms of logarithmic or polylogarithm (aka Jonquière) functions. The power-law exponent is a property that serves as an additional data fitting parameter. For the same initial slope, the modified isotherms deviate from the BET isotherm downwards, and the deviation increases with the exponent. Comparisons with some published isotherms obtained experimentally on cement pastes show that the present modification of the BET theory for hindered adsorption goes in the right direction. Detailed calibration of the theory and an extension for indirect communication of vapor molecules with the molecules adsorbed in nanopores less than a few nm wide will require further research.

**Key Words:** Adsorption isotherm, free adsorption, BET theory, hindered adsorption, evaporation and condensation, variation of adsorption surface, statistical analysis, capillary condensation theory, pore size distribution, polylogarithm, Jonquière functions.

**Introduction and Basic Concepts**

Adsorption of gases or vapors in multimolecular layers in porous solid is generally described by the classical BET theory, formulated in 1938 by Brunauer, Emmett and Teller (rumored to stem from a back-of-the envelope calculation of Edward Teller during a lunch) \([1, 2, 3]\). One important application of the BET has been the water desorption and adsorption in cement hydrates and concrete, which is here the main application in mind, although a similar problem arises, e.g., in activated carbon fibers formed by crystallite graphite sheets \([4]\). Various useful improvement of the BET theory, particularly its extensions to the capillary range, have been formulated \([5, 6, 7, 2, 8, 9, 10, 11, 12]\), but the effect of varying nanopore sizes on the area exposed to vapor, important for water in concrete, seems to have eluded attention.

The BET theory assumes that the number of molecular layers is unhindered, which requires wide enough pores. The number of adsorbed water layers containing significant mass

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increases with the vapor pressure, \( p \), or relative humidity \( h = p/p_{\text{sat}} \) and, for high enough \( h \), there can be up to 5 layers with significant adsorbed mass, which gives the approximate maximum thickness of 1.335 nm \( (p_{\text{sat}} = p_{\text{sat}}(T) = \text{saturation vapor pressure, a function of } T) \). This means that, in nanopores less than 2.67 nm wide (which constitute the major part of pore volume in cement hydrates), and for not too small \( h \), the adsorption layers on the opposite pore surfaces touch and fill the pore completely.

In materials with multiscale nanoporosity, such as concrete, the maximum thickness of nanopores filled by adsorbed water molecules decreases with decreasing \( h \) (Fig. 2b,c). When \( h \) exceeds the value at the limit of complete filling, the adsorption layer is hindered from developing its full thickness, and such a hindered adsorbed water layer (sometimes less fittingly also called the "interlayer water") develops a significant transverse pressure, called the disjoining pressure \([13, 14, 15, 16, 17, 18]\). The hindered adsorbed water requires us to distinguish two simple limiting cases:

1. In thin enough nanopores, less than a few nanometers thick, the adsorbed water molecules are restricted by solid surface forces and cannot communicate with the vapor in larger (capillary) pores directly. The adsorbed water molecules can communicate with water vapor in the larger pores only indirectly, by surface diffusion along the adsorption layers. The surface diffusion process is far slower than the process of direct adsorption from vapor on the adsorption layer surface exposed to vapor. Consequently, for the wetting or drying of porous specimens, which are sufficiently thin so that the delay due to macro-diffusion through the specimen is negligible, the water in the nanopores, whether filling the nanopores fully or partially, may be considered to be almost immobile. In this limiting case, which will be the object of the present analysis, the mathematical generalization of the BET theory is not difficult. One can ignore diffusion along the solid surface of the nanopores and deal only with the direct exchange of the adsorbate (water) molecules between the vapor and adsorption layers (which is why the term "direct" appears in the title).

2. The opposite case is a very slow drying or wetting, which allows the surface diffusion of hindered adsorbed water along the nanopores to run its course and come to a standstill. This limiting case should also be analytically tractable, in a way suggested in the Appendix. But more research is needed.

The mathematical derivation of the BET theory \([1, 3]\) is valid only for free, rather than hindered adsorbed layers \([12]\). This derivation is valid only when the surface, of area \( A' \), of the multimolecular adsorption layer in contact with the vapor is equal to be adsorbent area \( A \) and is independent of the number of layers. However, in materials such as cement hydrates, there are nanopores of highly variable width (Fig. 2b) and nanopores of uniform but very different widths (Fig. 2c). Consequently, the vapor exposed area, \( A' \), in cement hydrates and some other nanoporous materials must decrease significantly as \( h \) increases. In the limit case of sufficiently fast wetting or drying, in which the filling of the thin nanopores cannot change significantly, as stipulated at the outset (case 1), the decrease of \( A' \) may be described by an area reduction factor, \( \beta_n \), which depends on the number, \( n \), of multimolecular layers and reduces the full area \( A \) of the bare (or dry) internal pore surface per unit volume of the porous material (Fig. 2a), i.e.

\[
A' = \beta_n A \quad (n = 0, 1, 2, 3, \ldots, \beta_0 = 1)
\]
Here $\beta_n$ is a decreasing sequence; see Fig. 2 (in cement paste, $A \approx 500 \text{ m/cm}^3$, which implies the average pore width to be about $0.5 \text{ nm}$[12], or about two water molecules).

As for the hindered adsorption layers, which fill the nanopores completely (and are not thicker than $2.67 \text{ nm}$), we may assume that the migration of adsorbate (water) molecules along these layers (Fig. 2b,c) is so slow that it does not intervene appreciably with the rates of adsorption, evaporation and condensation on the surface in contact with vapor.

The decrease of the surface area of multimolecular adsorption layers with increasing number $n$ of the layers may be schematically represented as shown in Fig. 2a. Each horizontal line represents adsorbate volume that is equivalent to one molecular layer (the regular arrangement of molecules is, of course, only a mean idealization of a constantly varying random arrangement of molecules). The first layer occupies area $A$ of the bare adsorbent surface. For increasing $n$, we imagine the dashed lateral constraint to reduce the area of each molecular layer from $A$ to $A' = \beta_n A$, where $\beta_n (n = 1, 2, 3, ...)$ is a monotonically decreasing sequence, such that $\beta_0 = 1$ and $\beta_n > 0$ for all $n$.

A certain restriction on the surface area exposed to vapor was formulated, in 1940 by Brunauer et al.’s[2]. They generalized the BET theory to take into account two-sided adsorption layers on opposite parallel planar walls of a nanopore. The interference of the opposite twp-sided adsorption layers causes that the area exposed to vapor in the nanopore decreases as the adsorbate volume increases and vanishes as the nanopore gets full. A decrease of the area exposed to vapor also features in the present formulation, but that is where the similarity ends. Here, most of the increase of the exposed area with the multilayer thickness has a different source, explained by Fig. 1b,c. In [2]. This increase is achieved not by growth of the adsorbate volume in filled nanopores of varying width, but by a denser random filling of a nanopore of constant width (a pore between two parallel plates; see Fig. 1b), or Fig. 4 in [2]. The main problem with [2] is the disregard of the vastly increased resistance to the movement of adsorbate molecules along the nanopore, which occurs by surface diffusion. Unlike here, the statistical analysis in [2] implies nanopores of uniform width, which is true for some materials (e.g., charcoal or crystalline dolomite rocks) but is far from true for the cement hydrates. As another difference, in [2] it is considered that when the molecular layers growing from opposite surfaces of a planar nanopore touch, their heat of liquefaction increases, while this increase is not modeled. The calculated isotherm, given by equations (E) and 16 in [2], is much more complicated than what is obtained here. Brunauer et al.’s aim was to describe the isotherms of types IV and V, as defined in figure 1 of [2][3], while here we aim at the isotherms of types I, II and III (although a simple adjustment could also fit types IV and V). The theory in [2], based on statistics of adsorption in a planar nanopore of constant width, cannot be extended to the capillary range, while the present theory can.

**Adsorption under Lateral Constraint of Hindered Adsorption Layers**

Adsorption is a random process in which water molecules constantly enter the adsorption later, stay there for a certain time called the lingering time (about $10^{-9} \text{ s}$[20]) and then exit into the vapor. In equilibrium, the number of water molecules within the layer is at
any time is, macroscopically, exactly the same. Although the arrangement of molecules at
any moment varies and looks rugged as shown in Fig. 2c, one can define a precise effective
thickness \( \delta_{ef} \) as the volume occupied by all the water molecules per unit base area.

Let us now follow as closely as possible the original derivation of the BET theory [1, 3],
though with some vital differences. With a focus on hydrated cement, let us consider that
the adsorbate is water, although it could be some other substances. Let \( A \) be the total base
area of the adsorbent base, corresponding to the internal pore surface in a porous materials,
and let \( \alpha_n \) be the exposed coverage density in the \( n^{th} \) adsorption layer, i.e., the area fraction
of the adsorbed (or water) molecules that are exposed to vapor in the \( n^{th} \) layer (Fig. 2h).

Consider now a small area \( dA \) of the adsorbent base. The rate (or probability) of the
water vapor molecules condensing (or getting adsorbed) on top of the \((n-1)^{st}\) layer is
\( q_1 dA = a_n \alpha_{n-1} p dA \) where \( p \) is the vapor pressure and \( a_n \) is a constant (to be determined later).

The rate (or probability) of the vapor molecules condensing from the vapor into the \( n^{th} \)
layer (i.e., on top of the \((n-1)^{th}\) layer), is
\( q_2 dA = b_n \alpha_n e^{-Q/RT} dA \) where \( b_n \) is another constant (to be determined later),
\( T = \) absolute temperature, \( R = \) gas constant, and \( Q = \) activation energy. For the first layer, \( n = 1 \), \( Q = Q_a = \) heat of adsorption (which is dissipated upon upon severance of van der Waals bonds at the adsorbent surface as water molecules escape from the surface). For all the layers except the first, it is assumed, same as in the BET theory, that \( Q = Q_l = \) heat of liquefaction, which means that the van der Waals forces of the adsorbent surface are assumed to have no appreciable effect beyond the first layer.

In thermodynamic equilibrium, both rates (or probabilities) must be equal, i.e., \( q_1 = q_2 \),
and so
\[
\text{for } n = 1: \quad a_1 \alpha_0 p = b_1 \alpha_1 e^{-Q_a/RT} \\
\text{for } n = 2, 3, 4, \ldots: \quad a_n \alpha_{n-1} p = b_n \alpha_n e^{-Q_l/RT}
\]
which means that, for each layer, the density (or probability) \( q_1 \) of the rate of adsorption or
condensation must be equal to and the density (or probability) \( q_2 \) of the rate of evaporation.

Note that the area reduction factors, \( \beta_n \), must not appear in these equations because
they represent densities, per unit area of the base layer, and are independent of the lateral
spread of that layer defined by these factors. However, these area reductions factors, which
represent lateral constraints on the layer areas (Fig. 3), intervene in the global constraints,
which are:
\[
A = \sum_{n=0}^{\infty} \beta_n (\alpha_n A) \quad (4)
\]
\[
v = \delta_1 \sum_{n=0}^{\infty} n \beta_n (\alpha_n A) \quad (5)
\]
where \( \delta_1 = \) effective thickness of monomolecular adsorbed layer (representing the volume, \( v_m \),
of that layer per unit area of adsorbent surface), and \( v = \) total volume of adsorbate over area
\( A \). Eq. (4) means that the sum or the top areas of the random columns of \( n \) water molecules,
for all possible column heights \( n \) (Fig. 3b), must be equal to the adsorbent base area \( A \).
Eq. (5) sums the volumes of all the columns of water molecules of various random heights $n$ (the volume and area per water molecule are omitted in these equations because they later cancel out). The ratio defines the effective thickness of the adsorption layer. Taking the dimensionless ratio $v/A\delta_1$ and setting $A\delta_1 = v_m = $ volume of a full monomolecular layer, we obtain the overall lateral constraint:

$$\frac{v}{A\delta_1} = \frac{v}{v_m} = \frac{\sum_{n=0}^{\infty} n\beta_n \alpha_n}{\sum_{n=0}^{\infty} \beta_n \alpha_n}$$

which represents the key difference from the BET theory [1] and its extension to two-sided adsorption [2].

Assuming that the van der Waals forces of solid surface do not reach beyond the first molecular layer, and noting that a molecule entering of the layers beyond the first essentially undergo liquefaction, we may consider the ratios $b_n/\alpha_n$ to be constant for $n > 1$, i.e.,

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \frac{b_2}{a_2} = \ldots = g$$

where $g$ is a constant. Let us now define two variables:

$$y = \frac{a_1}{b_1} p e^{Q_a/RT}$$

$$h = \frac{p}{g} e^{Q_l/RT}$$

(as shown later, $h = p/p_{sat} =$ relative humidity of the vapor). With these notations,

$$\alpha_1 = y\alpha_0$$

$$\alpha_n = h\alpha_{n-1} = h^2\alpha_{n-2} = h^3\alpha_{n-3} = h^{n-1}\alpha_1 = yh^{n-1}\alpha_0 = c_T h_n \alpha_0$$

in which

$$c_T = \frac{y}{h} = \frac{a_1}{b_1} g e^{\Delta Q/RT}, \quad \Delta Q = Q_a - Q_l$$

where always $Q_a > Q_l$. The saturation humidity, $p = p_{sat}$, is obtained for $v \to \infty$. This corresponds to $h = 1$ and shows that the meaning of notation $h$ is indeed the relative humidity of pore vapor, i.e.,

$$h = \frac{p}{p_{sat}}$$

and also that, according to Eq. [9], $(p_{sat}/g)e^{Q_l/RT} = 1$ or

$$g = p_{sat}(T) e^{Q_l/RT}$$

So we may conclude that

$$c_T = c_0 e^{Q_l/RT}$$

where $c_0$ is an empirical calibration parameter (close to 1).

Substitution of Eq. [10] and [11] into Eq. [6] now furnishes for the sorption isotherm the result:

$$\frac{v}{v_m} = \frac{\theta(h, T)}{c_T \sum_{n=1}^{\infty} \beta_n \alpha_n}$$

For the special case that $\beta_n = 1$ for all $n$ (no hindered adsorption), this formula yields the BET isotherm.
Isotherms Obtained for Various Area Reduction Factors

Because of their self-similarity, power functions of $n$ appear to be a suitable choice for $\beta_n$ and, as it turns out, the infinite sums can be evaluated analytically. The simplest choice, satisfying the condition that $\beta_0 = 1$, is

$$\beta_n = \frac{1}{1+n}$$

for which

$$\sum_{n=1}^{\infty} \beta_n h^n = \sum_{n=1}^{\infty} \frac{h^n}{1+n} = -\frac{h + \ln(1-h)}{h}$$

and

$$\sum_{n=1}^{\infty} \beta_n n h^n = \sum_{n=1}^{\infty} \frac{n h^n}{1+n} = -\frac{h \ln(1-h) - h - \ln(1-h)}{h(1-h)}$$

Eq. (16) then yields, for the hindered isotherm, the final expression (Fig. 3a):

$$\theta(h, T) = c_T \frac{h + \ln H - h \ln(H)}{H(h - c_T \ln H - c_T h)}, \quad H = 1 - h$$

Fig. 3a shows a comparison of the plot of this hindered isotherm with the BET isotherm. Note that, similar to the BET isotherm, this isotherm cannot be valid in the capillary range ($h > 0.85$), unless a finite number $n$ is considered. This is obvious since $\lim_{h \to 1} \theta = \infty$.

For the 5th molecular layer, the area reduction factor due to hindered adsorption is $\beta_5 = \frac{1}{16}$. Whether this is realistic will depend on experiment (or MD simulations).

Eq. (17) for $\beta_n$ does not have any fitting parameter to optimize the fit of experimental adsorption data, and so it would be by luck if it provided a good fit of some experimental data. More generally, we can introduce a fitting parameter, $r$, such that

$$\beta_n = \frac{1}{(1+n)^r}$$

Varying $r$, one has a continuous transition to the BET theory, which is attained for $r \to 0$. For arbitrary $r$, the isotherm can be expressed in terms of a special function, the polylogarithm (aka Jonqui`ere’s function), which is denoted by $Li_r(h)$ (and is valid when $|h| < 1$). We have (Fig. 3a):

$$\sum_{n=1}^{\infty} \beta_n h^n = \sum_{n=1}^{\infty} \frac{h^n}{(1+n)^r} = \sum_{n=0}^{\infty} \frac{h^n}{(1+n)^r} - 1 = \frac{Li_r(h)}{h} - 1$$

and

$$\sum_{n=1}^{\infty} \beta_n n h^n = \sum_{n=1}^{\infty} \frac{n h^n}{(1+n)^r} = \frac{Li_{r-1}(h) - Li_r(h)}{h}$$

Hence

$$\theta(h, T) = c_T \frac{Li_{r-1}(h) - Li_r(h)}{h + c_T (Li_r(h) - h)}$$

Another, simpler, way is to assume $\beta_1 (\leq 1)$ to be a free fitting parameter, and consider that the subsequent area reduction factors are:

$$\beta_n = \frac{\beta_1}{n}, \quad n = 1, 2, 3, 4, ...$$
As a result, the summed series and \( \theta \) function are followed (Fig. 3b):

\[
\begin{align*}
\sum_{n=1}^{\infty} \beta_n h^n &= \sum_{n=1}^{\infty} \frac{\beta_1 h^n}{n} = -\beta_1 \ln(1-h) \\
\sum_{n=1}^{\infty} \beta_n h^n &= \sum_{n=1}^{\infty} \frac{\beta_1 h^n}{n} = \beta_1 \frac{h}{1-h}
\end{align*}
\]

Hence

\[
\theta(h, T) = \frac{c_0 \beta_1 h}{(1-h)\left(1-c_0 \beta_1 \ln(1-h)\right)}
\]

Another alternative is to add another fitting parameters \( r \) together with \( \beta_1 \), which would be:

\[
\beta_n = \frac{\beta_1}{n^r}, \quad n = 1, 2, 3, 4, ...
\]

For \( \beta_1 \to \beta_0 = 1 \) and \( r \to 0 \), one can have again a continuous transition to the BET theory (Fig. 3b).

\[
\begin{align*}
\sum_{n=1}^{\infty} \beta_n h^n &= \sum_{n=1}^{\infty} \frac{\beta_1 h^n}{n^r} = \beta_1 \text{Li}_r(h) \\
\sum_{n=1}^{\infty} \beta_n h^n &= \sum_{n=1}^{\infty} \frac{\beta_1 h^n}{n^r} = \beta_1 \text{Li}_{r-1}(h)
\end{align*}
\]

Leading to

\[
\theta(h, T) = \frac{c_0 \beta_1 \text{Li}_{r-1}(h)}{1 + c_0 \beta_1 \text{Li}_r(h)}
\]

If the experimental (or MD) data are abundant enough to optimize more fitting parameters, \( \beta_1, \beta_2, \) and \( r \), one may consider that

\[
\beta_n = \frac{\beta_2}{(n-1)^r}, \quad n = 2, 3, 4, ...
\]

For \( r = 1 \):

\[
\begin{align*}
\sum_{n=1}^{\infty} \beta_n h^n &= \beta_1 h + \sum_{n=2}^{\infty} \frac{\beta_2 h^n}{n-1} = \beta_1 h - \beta_2 h \ln(1-h) \\
\sum_{n=1}^{\infty} \beta_n h^n &= \beta_1 h + \sum_{n=2}^{\infty} \frac{\beta_2 h^n}{n-1} = \beta_1 h + \beta_2 \frac{h + h \ln(1-h) - \ln(1-h)}{1-h}
\end{align*}
\]

Therefore, the sorption isotherm can be obtained as (Fig. 3c):

\[
\theta(h, T) = \frac{c_0 \beta_1 h H + \beta_2 (h + h \ln H - \ln H)}{(1-h)\left(1 + c_0 \beta_1 h - \beta_2 h \ln H\right)}, \quad H = 1 - h
\]

A common feature to all of the foregoing functions is that the reduced area vanishes for \( n \to \infty \). Physically this is not objectionable since the adsorption and hindered adsorption are negligible for \( n > 5 \). But it may be useful to introduce a second parameter \( \gamma \) which gives a finite reduced area for \( n \to \infty \) and thus makes it possible to control the initial changes from \( \beta_0 \) to \( \beta_2 \), etc. So we generalize Eq. (21);

\[
\beta_n = \gamma + \frac{1 - \gamma}{(1+n)^r}, \quad n = 0, 1, 2, 3, 4, ...
\]
\[ \sum_{n=1}^{\infty} \beta_n h^n = \sum_{n=1}^{\infty} \left[ \gamma + \frac{1 - \gamma}{(1 + n)^r} \right] h^n = \gamma \frac{h}{1-h} + (1-\gamma) \left( \frac{Li_r(h)}{h} - 1 \right) \] (38)

and

\[ \sum_{n=1}^{\infty} \beta_n n h^n = \sum_{n=1}^{\infty} \left[ \gamma + \frac{1 - \gamma}{(1 + n)^r} \right] n h^n = \gamma \frac{h(1-h)^2}{1-h} + (1-\gamma) \frac{Li_{r-1}(h) - Li_r(h)}{h} \] (39)

The resulting sorption isotherm is shown in Fig. 3d:

\[ \theta(h, T) = c_T \frac{\gamma h^2 + (1-\gamma)H^2[Li_{r-1}(h) - Li_r(h)]}{hH^2 + c_T H[\gamma h^2 + (1-\gamma)H(Li_r(h) - h)]} \] (40)

However, not all analytical expressions can be obtained when \( \beta_n \) is a general decreasing function of \( n \). Exponential functions, for example, are not suitable. For \( \beta_n = e^{-\beta_1 n} \), the sum in the denominator of Eq. (16) converges only if \(|h| < e^{-\beta_1} \), and the sum in the numerator cannot be expressed in terms of any known function. Besides, whereas numerical summation of the first few significant terms would be no problem, the exponential decay might be too fast for characterizing nanopore structures. Unlike the power functions, the exponentials are not self-similar, which means that some characteristic nanopore size would have to exist, but none can be identified.

Another way to compare the foregoing functions \( \theta(h, T) \) is the initial slope. This slope can be determined and compared against BET theory to show how fast the restriction on free surface area develops. If this slope deviates significantly from the BET theory, one can infer that a large amount of pore space has a width on the order of nanometer scale. However, if it is close to the initial slope of BET curve, then one can say that the first few layers (which are also dominant ones in the adsorption regime) are quite free to develop. Such initial behavior can be obtained if we set the parameter \( \beta_1, \beta_2 \) in Eqs. (28), (32), (36) close to 1.

In general, \( \theta(h, T) \) can be easily computed by evaluating, numerically, the sums in Eq. (16). Only the terms for \( n = 0, 1, 2, ... 5 \) need to be computed since the subsequent terms are negligible.

Unlike the BET isotherm, none of foregoing isotherms is amenable to linear regression. Nevertheless, the isotherm parameters can be identified from sorption data almost instantly, by using optimum fitting of the measured isotherm with a powerful nonlinear optimization algorithms such a the Levenberg-Marquardt and using the BET isotherm as the initial estimate. This isotherm is a special case for \( r \to 0 \). Compared to [2], the present isotherms are not only more generally applicable but also much simpler.

Brunauer et al. [2, 3] distinguished 5 types of isotherm shapes. The present isotherm formulae are of type II. However, with the present method, a transition between different sorption isotherm types are possible. For example, for \( r \to \infty \) in Eq. (29), one gets the classical Langmuir isotherm for monomolecular adsorption layers. When \( c_T \) is very small, i.e., the adsorbent-solid interaction is very weak, the type III isotherm is retrieved. By proper calibration of \( \beta_n \) and exponent \( r \) in Eq. (21), types IV and V can also be reproduced.
Qualitative Comparisons with Some Previously Observed or Simulated Isotherms

To illustrate the behavior and usefulness of the present theory, the predicted isotherms and BET isotherms need to be compared with experiments in which hindered adsorption is likely to happen. This can be either a normal Portland cement paste with low water-cement ratio or various special types of cement with extra minerals or crystals to be formed. In these adsorbents, the C-S-H platelets or needles grow and create nanopores in which full adsorption layers exposed to vapor cannot develop. Using the same procedure as in [2], the \( c_T \), the monomolecular layer volume and mass, \( v_m \) and \( u_m \) (characterized as volume or mass adsorbed per 1 gram of dry sample), were obtained by fitting the regime of low relative humidity with BET theory. After that, the remaining relevant parameters (depending on which function was used) were fitted until the least-square error of fit was minimized.

Wang et al.’s [21] studied a compacted pore structure of phosphoaluminate cement (PAC) paste with water-cement ratio \( w/c = 0.32 \). Under scanning electron microscopy (SEM) image, the formation of cotton-shaped gels was observed, resulting in relatively low porosity and small pore sizes. As a result, Fig. 4a displayed a significant deviation from the BET isotherm above \( h \approx 0.25 \). A better match if obtained by fitting to these data the present isotherm with function \( \beta_n \) given be Eq. [21] with parameters \( \beta_1 = 0.998 \) and \( r = 0.986 \). Obviously, the fit is better for \( h > 0.25 \).

In another experiment, Powers and Brownyard [22] measured adsorption for a type IV cement paste with \( w/c = 0.309 \) and the equivalent age of \( t_e \approx 1 \) year. Up to 0.5, BET gave a good fit, but overestimated the isotherm for \( h > 0.5 \); see Fig. 4b.

Conclusions

1. Because the area of a multimolecular hindered adsorbed layer increases with the relative humidity of vapor, the area of the free (or unhindered) adsorption layers exposed to pore vapor decreases with the thickness of the multimolecular adsorbed layer, and thus also with the increasing humidity of vapor in the pores.
2. The basic idea in extending the BET isotherm to nano-porous solids with hindered adsorption is to treat the transitions from free to hindered adsorption as lateral constraints imposing an area reduction factor that decreases from one molecular adsorption layer to the next.
3. The key point in the derivation of the isotherms is that the area reduction factors apply only to overall volume and area of the free adsorbed layers but not to the local rates of water evaporation, liquefaction and adsorption on the solid adsorbent surface.
4. Generally, the isotherm is obtained as the ratio of the sums of two infinite series.
5. Considering the area reduction factor to be inversely proportional to the layer number leads to a simple analytical formula for the sorption isotherm. A general inverse power-law dependence of this factor on the layer number is also analytically tractable, and yields the isotherm expressed in terms of polylogarithm (aka Jonqui`ere) functions. For the same initial slope, the resulting isotherms deviate from the BET isotherm downward. The deviation grows with increasing exponent.
6. The inverse power law exponent is an additional empirical parameter providing flexibility in test data fitting. Excluding the first layer from the power law can provide another fitting parameter.

7. Qualitative comparisons with some published isotherms observed experimentally on cement pastes indicate that the present theory modifies the BET isotherm in the right direction.

8. The present analysis applies only to the drying or wetting that is not so slow as to allow significant mass exchange between water vapor and hindered adsorbed water in the nanopores less than 3 nm wide.

Appendix. Comment on sorption slow enough for all nanopores to reach equilibrium

To consider this case, the sorption isotherm \( \theta(h, T) \) may be redefined to represent only the volume of the free adsorbed layers directly exposed to vapor. The total relative volume of adsorbed water may be, in theory, approximated as

\[
\theta_{\text{total}}(h, T) = \theta(h, T) + 2H(h - h_n)[1 - \beta_n(h)]
\]

where \( H \) now represents the Heaviside step function and \( h_n \) is the vapor humidity at which nanopores \( 2n \) molecules wide, in equilibrium, completely filled by \( 2n \) molecular layers of the adsorbate. This case, however, requires further research.

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References

[1] Stephen Brunauer, Paul Hugh Emmett, and Edward Teller. Adsorption of gases in multi-molecular layers. *Journal of the American chemical society*, 60(2):309–319, 1938.

[2] Stephen Brunauer, Lola S Deming, W Edwards Deming, and Edward Teller. On a theory of the van der waals adsorption of gases. *Journal of the American Chemical society*, 62(7):1723–1732, 1940.

[3] S. Brunauer. *The adsorption of gases and vapors, Vol I - Physical Adsorption*. The Adsorption of Gases and Vapors. Princeton University Press, 1943.

[4] K Kaneko, C Ishii, M Ruike, et al. Origin of superhigh surface area and microcrystalline graphitic structures of activated carbons. *Carbon*, 30(7):1075–1088, 1992.

[5] Aleksej V Lykov and Karl Steffes. *Transporterscheinungen in kapillarporösen Körpern*. Akad.-Verlag, 1958.
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[6] P Freiesleben Hansen. Coupled moisture/heat transport in cross sections of structures. *Beton og Konstruktionsinstituttet (BKI), Denmark*, 1985.

[7] Hartwig M Künnzel. Simultaneous heat and moisture transport in building components. *One-and two-dimensional calculation using simple parameters*. IRB-Verlag Stuttgart, 1995.

[8] Stephen Brunauer, Jan Skalny, and EE Bodor. Adsorption on nonporous solids. *Journal of Colloid and Interface Science*, 30(4):546–552, 1969.

[9] George Halsey. Physical adsorption on non-uniform surfaces. *The Journal of Chemical Physics*, 16(10):931–937, 1948.

[10] Arne Hillerborg. A modified absorption theory. *Cement and Concrete Research*, 15(5):809–816, 1985.

[11] Yunping Xi, Zdeněk P Bažant, and Hamlin M Jennings. Moisture diffusion in cementitious materials adsorption isotherms. *Advanced cement based materials*, 1(6):248–257, 1994.

[12] Zdeněk P Bažant and Milan Jirásek. *Creep and Hygrothermal Effects in Concrete Structures*, volume 225. Springer, 2018.

[13] BV Deryagin. Theory of capillary condensation and other capillary phenomena with allowance for wedging effect of polymolecular liquid films. *Zhurnal fizicheskoi khimii*, 14, 1940.

[14] TC Powers. Some observations on the interpretation of creep data. *Bulletin RILEM (Paris)*, 33:381–391, 1966.
[15] ZP Bažant. Thermodynamics of hindered adsorption and its implications for hardened cement paste and concrete. *Cement and Concrete Research, 2*(1):1–16, 1972.

[16] ZP Bažant. Thermodynamics of interacting continua with surfaces and creep analysis of concrete structures. *Nuclear engineering and design, 20*(2):477–505, 1972.

[17] Zdeněk P Bažant and Martin Z Bazant. Theory of sorption hysteresis in nanoporous solids: part i: snap-through instabilities. *Journal of the Mechanics and Physics of Solids, 60*(9):1644–1659, 2012.

[18] Martin Z Bazant and Zdeněk P Bažant. Theory of sorption hysteresis in nanoporous solids: Part ii molecular condensation. *Journal of the Mechanics and Physics of Solids, 60*(9):1660–1675, 2012.

[19] Jia-Liang Le, Zdeněk P Bažant, and Martin Z Bazant. Unified nano-mechanics based probabilistic theory of quasibrittle and brittle structures: I. strength, static crack growth, lifetime and scaling. *Journal of the Mechanics and Physics of Solids, 59*(7):1291–1321, 2011.

[20] Jan Hendrik Deboer. *The dynamical character of adsorption*, volume 76. LWW, 1953.

[21] Weilun Wang, Peng Liu, Ming Zhang, Jiashan Hu, and Feng Xing. The pore structure of phosphoaluminate cement. *Open Journal of Composite Materials, 2*(03):104, 2012.

[22] Treval Clifford Powers and Theodore Lucius Brownyard. Studies of the physical properties of hardened portland cement paste. In *Journal Proceedings*, volume 43, pages 101–132, 1946.