Models of Sigmoid Equilibrium Moisture Sorption Isotherms With and Without the Monolayer Hypothesis

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Abstract

Among the numerous moisture sorption models, the GAB, an expanded version of the BET equation originally derived for inert gases adsorption on solid surfaces, is the most prominent. Both models are based on distinction between the adsorbate molecules settling on the bare surface in a monolayer (Langmuir adsorption) and those settling on already absorbed molecules forming multilayers. The BET theory has been successfully used to determine porous catalysts' and fine powders' specific surface area to this day. In contrast, applying the BET and GAB equations to water vapor sorption by solid foods (and non-foods) has at least three major problems: The calculated food powders' specific surface area is independent of their particle size; the expected shoulder in foods' enthalpy vs. moisture plot is absent; and there is a huge discrepancy between the specific surface areas calculated from moisture sorption isotherms and those of nitrogen. An alternative modeling approach posits the non-existence of a water monolayer, and suggests that moisture sorption is governed by at least two simultaneous mechanisms having different scaling exponents. Mathematical analysis and comparison of the resulting sorption models with the GAB equation show that they produce practically indistinguishable moisture sorption isotherms even with the same number of adjustable parameters. They also demonstrate that the sigmoid shape of a moisture sorption isotherm does not contain enough information to identify and quantify the underlying sorption mechanisms, and that a model's good fit by statistical criteria in itself does not validate mechanistic assumptions.

Keywords Water · BET · GAB · Monolayer · Surface area · Chemical sorption

Introduction

Because of the crucial role water plays in food safety, stability, processing and packaging, mathematical description of foods' moisture sorption isotherms has been a perennial topic in food research for more than half a century [4, 5, 24]. The same can be said about several other disciplines, from pharmacology and powder technology to wood and soil sciences. Not surprisingly, there are so many publications reporting on the application and comparison of sorption models, traditional and novel, that they are too numerous to be all cited and assessed. [At the time of these lines writing, a Google Scholar search for 'moisture sorption isotherm models for food' has rendered more than 35,000 hits, over 17,000 of them since 2015.] This review is neither an attempt to rate moisture sorption models nor to compare their fit to reported or new data; abundant information of this kind can be found in several of the cited publications.

Moisture sorption is a subject covered in the curriculum of most if not all Food Science and Food Engineering academic programs and hence need no introduction to the journal's readers. It is amply discussed not only in numerous research papers but also in many review articles, books and book chapters, widely available both in print and on the Internet. What follows is therefore neither a literature guide to publications on the development and use of sorption models in foods characterization nor a summary or overview of the physical chemistry of water sorption. What this article provides is a formalistic mathematical analysis of the most common sorption models' properties with emphasis on their interpretation and implications. The GAB model, an offshoot of the famous BET equation, is arguably the most widely discussed moisture sorption model in the food literature. Therefore, special attention will be given to the 'water monolayer concept' from which these two models and their other offshoots have been derived.

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A food's isothermal equilibrium moisture sorption curve is commonly presented as a plot of its % moisture content, $m(a_w)$, expressed on dry basis, i.e., gram water per 100 g dry matter, vs. its water activity a_w (dimensionless) at a chosen constant temperature. There are different kinds of equilibrium sorption curves, but, particularly in foods containing a substantial amount of proteins and/or carbohydrates (sugars are a notable exception), the curve has a characteristic sigmoid shape of the kind, shown schematically in Fig. 1, known as Type II isotherm according to the International Union of Pure and Applied Chemistry (IUPAC).

When a food's sample exposed to an atmosphere having constant relative humidity reaches constant weight, usually after about 48 h or longer, the corresponding moisture contents is assumed to be the equilibrium moisture content and is frequently reported as such. Whether foods, which are chemically and/or biologically active, can actually reach true equilibrium is a debatable issue. One cannot dismiss offhandedly the possibility that had the moisture determination method been much more sensitive and accurate, weight changes after longer exposure times than those used would be detected. But, since very long exposure of a food especially to intermediate and high relative humidities can result in its biological or chemical deterioration, the equilibrium issue might not be settled even experimentally. However, since our discussion focuses on the mathematical properties of sorption models and not on the foods themselves, what follows will refer to equilibrium moisture contents regardless of how the 'equilibrium' is defined and determined. Also, it is well known and amply documented that the equilibrium moisture sorption curves of many foods show hysteresis, i.e., they have a different shape when determined by sorption or desorption. But, here again, we will not address the hysteresis possible causes and their manifestations and deal only with the mathematical models that describe equilibrium sorption curves regardless of how they have been determined experimentally.

Comparisons of several models' fits to the same water sorption datasets are ubiquitous in the food literature, e.g., [2, 3, 9–12, 15–17,19, 27, 29]. In many of these comparisons, several different models, having from 2 to 4 adjustable parameters, show similar fit as judged by statistical criteria. Thus, when the fit of two or more models is close, it is frequently difficult to establish whether the slightly better or worse fit is primarily due to the number of their adjustable parameters (the most likely), an accidental experimental scatter in the data or both, an issue to which we will return.

Mathematical Models of Sigmoid Moisture Sorption Isotherms

Isothermal moisture sorption curves, as already been stated, have been described by an impressive number of different mathematical models [2, 3, 5–10, 12, 17, 26–29, 31]. These models can be classified in different ways, for instance by the number of their adjustable parameters, 2, 3 or 4, whether they include a logarithmic, exponential or power term(s), whether they imply that at $a_w = 0$, $m(0) = 0$ and/or that at $a_w \rightarrow 1$, $m(1) \rightarrow \infty$. For our discussion, we will divide the existing sorption models into two groups only: empirical or semi empirical algebraic expressions having two or more adjustable parameters and models that have been derived from sorption kinetic considerations based on the hypothesis that there exists a water monolayer. The second group includes the BET and GAB models themselves, and their modified versions, which maintain the monolayer term in their equation.

Fig. 1 The sigmoid equilibrium moisture sorption isotherms of wheat flour, generated with the GAB equation parameters reported in [16]. Its two underlying hypothetical components are presented as dashed curves. Left (Type IIa)—based on the monolayer hypothesis; right (Type IIb)—constructed with the assumption of the water monolayer nonexistence
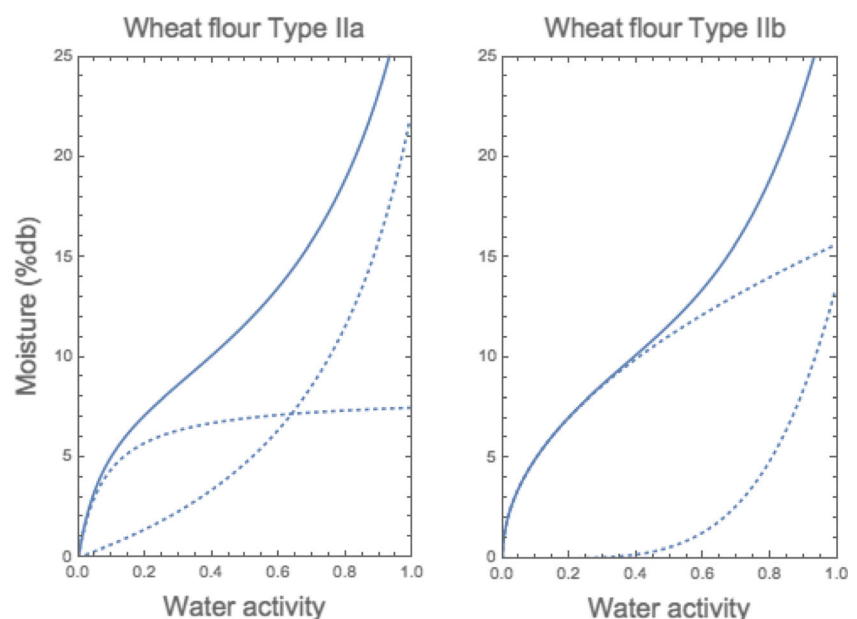
Empirical and Semi-empirical Two-Parameter Models

Among the 23 sorption models discussed by Iglesias and Chirife [12], the most familiar two-parameter models of the first kind are

Hasley's

$$m(a_W) = \left(-\frac{c}{Ln[a_W]}\right)^{1/n} \qquad (1)$$

Henderson's

$$m(a_W) = \left(-\frac{Ln[1-a_W]}{c}\right)^{1/n} \qquad (2)$$

Oswin's

$$m(a_W) = c\left(\frac{a_W}{1-a_W}\right)^n \qquad (3)$$

and Smith's

$$m(a_W) = c_1 + c_2 Ln[1-a_W] \qquad (4)$$

where the c's or n's are constants.

Having only two adjustable parameters, they all conform to the *parsimony principle*, which is related to Occam's (also spelled Ockham's) razor. However, such models might not always provide adequate fit to experimental data covering the entire water activity range ($0 \le a_w \le 1$), thus providing the rationale for the development of more elaborate models having three or more adjustable parameters. Theoretically, one would expect that *any* general moisture sorption model, regardless of its kind and number of parameters, should be consistent with the requirements that at $a_w = 0$, $m(0) = 0$ and that at $a_w = 1$ (pure water), $m(1) \rightarrow \infty$ (free condensation). In practice, these two requirements are not always met, especially the second. This is probably because, at very high water activity levels, $a_w \sim 0.98$ say, the moisture sorption curve's ascent rate is frequently not as steep as predicted (by extrapolation) by models that do satisfy the condition of $m(1) \rightarrow \infty$.

Notice that, from a purely formalistic viewpoint, the famous BET equation, when applied to water vapor adsorption by foods, can be considered a two-parameter sorption model expressed in the form:

$$m(a_W) = \frac{c_1 a_W}{(1+c_2 a_W)(1-a_W)} \qquad (5)$$

where c_1 and c_2 are the adjustable parameters. This model satisfies both conditions concerning $a_w = 0$ and $a_w = 1$.

Also notice that the Henderson and Oswin models, which too satisfy these two conditions, can be written in the form of a single power-law term

$$m(a_W) = cx^m \qquad (6)$$

where $x = Ln[1/(1-a_W)]$ or $x = a_W/(1-a_W)$, respectively. Replacing a_W in Eq. 5 by x, defined either way, creates an empirical version of the BET equation, which can be particularly suitable for *very high water activities* [23].

Empirical and Semi-empirical Three-Parameter Models

The fit of the above listed two-parameter models to experimental sorption data has been found satisfactory in many foods albeit not always for the entire water activity range, as mentioned. Improvement of these models' fit and/or extension of their applicable a_w range has been frequently accomplished by adding a third adjustable parameter to an existing equilibrium moisture sorption equation. Here are two examples [1]:

A modified Halsey model

$$m(a_w) = \left(\frac{-Exp[c_1+c_2 T]}{Ln[a_w]}\right)^{1/n} \qquad (7)$$

A modified Henderson model

$$m(a_w) = \left(-\frac{Ln[1-a_w]}{c_1+c_2 T}\right)^{1/n} \qquad (8)$$

where T is the temperature.

Other examples are the Ferro-Fantan, Chirife, Sancho & Iglesias model [2]

$$m(a_w) = \left(\frac{c_1}{Ln[c_2/a_w]}\right)^{1/n} \qquad (9)$$

and the modified Mizrahi model [30]

$$m(a_w) = \frac{c_1 + a_W(c_2 a_W + c_3)}{a_W - 1} \qquad (10)$$

An alternative has been to resort to the purely descriptive but very flexible third degree polynomial model, which in our context has the form [31]

$$m(a_w) = c_1 + c_2 a_w + c_1 a_w^2 \qquad (11)$$

This model coefficients' connection to the physics of the moisture sorption phenomenon is yet to be established. For polynomial models of higher degrees and their relation to the GAB equation, see [30]. The technical advantages of the polynomial models over most if not all the other three or more parameter models are that their parameters extraction from experimental data by regression does not require guessed initial values regardless of its degree, and that a solution is always guaranteed. Describing the equilibrium moisture sorption isotherms of dry food ingredients by a polynomial model

(of same or higher degree) has another advantage. It facilitates writing the governing equation to calculate the equilibrium water activity of their mixtures in a sealed container [21]. Here too there is no need to come up with any initial guess to solve the governing equation numerically, and the solution is reached practically instantaneously.

The BET Sorption Model

The BET equation is named after its authors Brunauer, Emmett and Teller. In 1938 they expanded the Langmuir model, which describes an inert gas molecules adsorption on a solid surface forming a layer one molecule thick. The BET theory accounts for the formation of a second and additional molecular layer in which the gas molecules are deposited on previously absorbed ones rather than on available sites on the bare solid surface. The theory was primarily developed for surface area determination of porous solids, particularly catalysts, and of very fine powders. For these two purposes, the BET theory has been widely and successfully used ever since.

Both the Langmuir and BET theories' starting point is that a given solid surface has a finite number of sorption sites at which an inert gas's molecules, the "adsorbate," can settle. The *number* of molecules that saturate all these available sites in a single layer, i.e., of molecules not settling on top of each other, determines the "monolayer value." Both the Langmuir and BET theories also assume that the adsorbate's molecules behave as an ideal gas.

Energetically [13, 22, 25], according to the BET theory, the heat involved in the monolayer creation is the net heat of sorption representing the affinity of the gas to the solid surface, to which the latent heat of evaporation (= heat of condensation) is added. It is assumed that, in the second and subsequent layers, where the adsorbate's molecules settle on molecules of their own kind, the process is equivalent to vapor condensation and hence the heat involved is just the absorbed gas's heat of evaporation. The manifestation of this ideal scenario is an enthalpy vs. moisture relationship of the kind shown schematically in Fig. 2. In reality, the transition between adsorption and condensation need not be as sharp as the model implies, and it is more likely represented, at least qualitatively, by the dashed curve, which is also shown in the figure—see [14].

Mathematical description of the above scenario is the famous BET equation for isothermal physical adsorption:

$$W(x) = \frac{W_m C x}{(1-x)(1 + (C-1)x)} \qquad (12)$$

where $W(x)$ is the amount of the absorbed gas, expressed as the adsorbate's volume, mass or moles at equilibrium for the gas's partial pressure $x = p/p_0$, W_m is the amount of gas adsorbed as a monolayer and C a dimensionless constant defined by the energy/temperature term
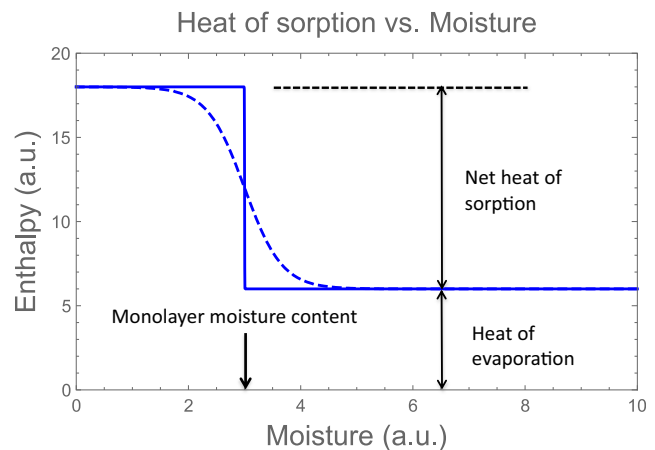

Heat of sorption vs. Moisture

Fig. 2 Ideal and non-ideal sorption enthalpy vs. moisture content plots from which the monolayer existence can be inferred

$$C = Exp\left[\frac{E_s - E_v}{RT}\right] \qquad (13)$$

where E_s is the total heat of sorption and E_v the latent heat of evaporation.

Notice that, if the individual adsorbate molecule's effective, i.e., projected area, is known, its multiplication by the number of the molecules in the monolayer (derived from W_m) renders the solid's surface area. This surface area can be readily converted into the porous solid's or fine powder's *specific surface area*, which is commonly expressed in m^2/g. Such a surface area determination is possible because the diameter and hence the projected area of individual gas molecules such as N_2, Ar, Kr or He and also H_2O, see below, are extremely small relative to the size of even very tiny structural pores and the microscopic irregularities of an actual solid surface. This allows the adsorbate molecules to practically cover the entire solid surface regardless of its microscopic topography and, in case of fine powders, regardless of their particles size and shape.

Eq. 12 can be linearized and written in the form

$$\frac{1}{W(x)(1/x-1)} = \frac{(C-1)x}{W_m C} + \frac{1}{W_m C} \qquad (14)$$

The linearity of an experimental $\frac{1}{W(x)(1/x-1)}$ vs. x plot, even if only observed at the lower end of the $W(x)$ vs. x relationship, has been traditionally considered the BET model's affirmation and used to extract the monolayer value, W_m, and the magnitude of the C constant, from the straight line's slope and intercept, a topic to which we will return.

Technical issues concerning experimental surface area determinations using absorbed inert gases are clearly outside the scope of this review. Nevertheless, it ought to be mentioned that, in contrast with water vapor sorption isotherms, which can be and are frequently determined at ambient or slightly

above or below ambient temperatures, the equilibrium sorption isotherms of the mentioned and other inert gasses are obtained at temperatures that are commensurate with their boiling points, which requires special instrumentation for their determination. The boiling points of nitrogen, argon, krypton and helium are about -196, -186, -153 and -269 °C, respectively. Their individual molecules' assumed projected areas are the following: N_2 about 0.162, Ar about 0.166, Kr about 0.195 and He 0.089 nm^2. The assumed H_2O molecule's projected area is about 0.106 nm^2, i.e., it is closest to that of He. It is about two-thirds of the N_2 and Ar molecules' areas and about half that of the Kr molecule. We will return to this issue when addressing the applicability of the BET equation and related models to water vapor sorption by foods and the question of whether molecular sieving may play a role in the discrepancy between foods' and other materials' specific surface area when calculated from nitrogen and water vapor sorption isotherms.

The GAB and Related Sorption Models

The GAB model named after Guggenheim, Anderson and Boer is an expansion of the BET equation [26, 27], and it too has been expanded, having at least six modified versions [27, 6]. When applied to foods' moisture sorption isotherms, the GAB model's most familiar presentation is in the form

$$W(a_w) = \frac{W_m C k a_w}{(1 - k a_w)(1 + (C-1) k a_w)} \quad (15)$$

where W_m is the monolayer value and C and k are the constants.

From a purely formalistic viewpoint, Eq. 15 is a three-parameter sorption model having the generic form

$$m(a_W) = \frac{c_1 a_W}{(1 + c_2 a_W)(c_3 - a_W)} \quad (16)$$

where the c's are temperature-dependent characteristic constants.

Unlike the original BET model (Eq. 5), the GAB model implies that as $a_W \to c_3 \neq 1$, $m(a_W) \to \infty$. Having this feature and three instead of two adjustable parameters, the GAB model usually has a better fit to experimental sorption data than the original BET model, and a larger range of applicability [27]. The GAB monolayer value can be extracted from experimental sorption data by nonlinear regression using Eq. 15 as a model. The same can be said about the BET monolayer calculation using Eq.12 as model and about the expanded versions of either.

The excellent fit of the GAB model to foods' moisture sorption isotherms data, frequently superior to that of other models, has been reported in numerous publications. Nevertheless, because neither the BET nor the GAB model

is unique, good fit by statistical criteria alone does not establish their validity as physical models. Demonstrations of the GAB model's interchangeability with other models can be examined with the freely downloadable Wolfram Demonstration http://demonstrations.wolfram.com/ComparisonOfFoodMoistureSorptionIsothermEquations whose screen display is shown in Fig. 3. (To run the Demonstration (and over 12,000 other Demonstrations to date), download the free Wolfram CDF Player following instructions on the screen.) In the particular configuration shown in the figure, there is an almost perfect fit of the two-parameter Oswin model to data generated with the three-parameter GAB equation with no scatter. Not all the two-parameter models have such an excellent fit for the shown data generated with the GAB model's particular parameter settings, let alone all the numerous GAB parameter combinations permitted by the program, of course. Nevertheless, there are still quite a few parameter combinations that, if applied to actual data with an experimental scatter, would be at least practically indistinguishable. The double power-law model, the last model choice in this Demonstration, almost always provides excellent fit as judged visually and by statistical measures ($r^2 > 0.99$). But, because the double power-law model has four adjustable parameters and the GAB model only three, this not surprising, another issue to which we will return.

Issues with the "Water Monolayer" Hypothesis

The notion that foods have a physical water monolayer has been widely accepted in the food literature. Being linked to what is known as "bound water," the concept has also been invoked to explain the role of water in food stability, a topic on which we will not dwell. Although certainly not new, the issue of whether there really exists a water monolayer in foods has never been satisfactorily settled. The main three reasons to doubt its reality are

1. Had the calculated water monolayer value represented a physical surface its magnitude in food powders should have increased dramatically as a result of particle size reduction.
2. Had the calculated monolayer had physical reality a plot of the heat of sorption vs. moisture content would have a shape of the kinds depicted in Fig. 2, i.e., having a noticeable shoulder from which its existence could be easily inferred. In reality, many such published plots have shapes more reminiscent of a continuous exponential decay or have a peak followed by exponential decay with no discernible shoulder.
3. When the specific surface area of solid foods has been determined from equilibrium moisture sorption data,

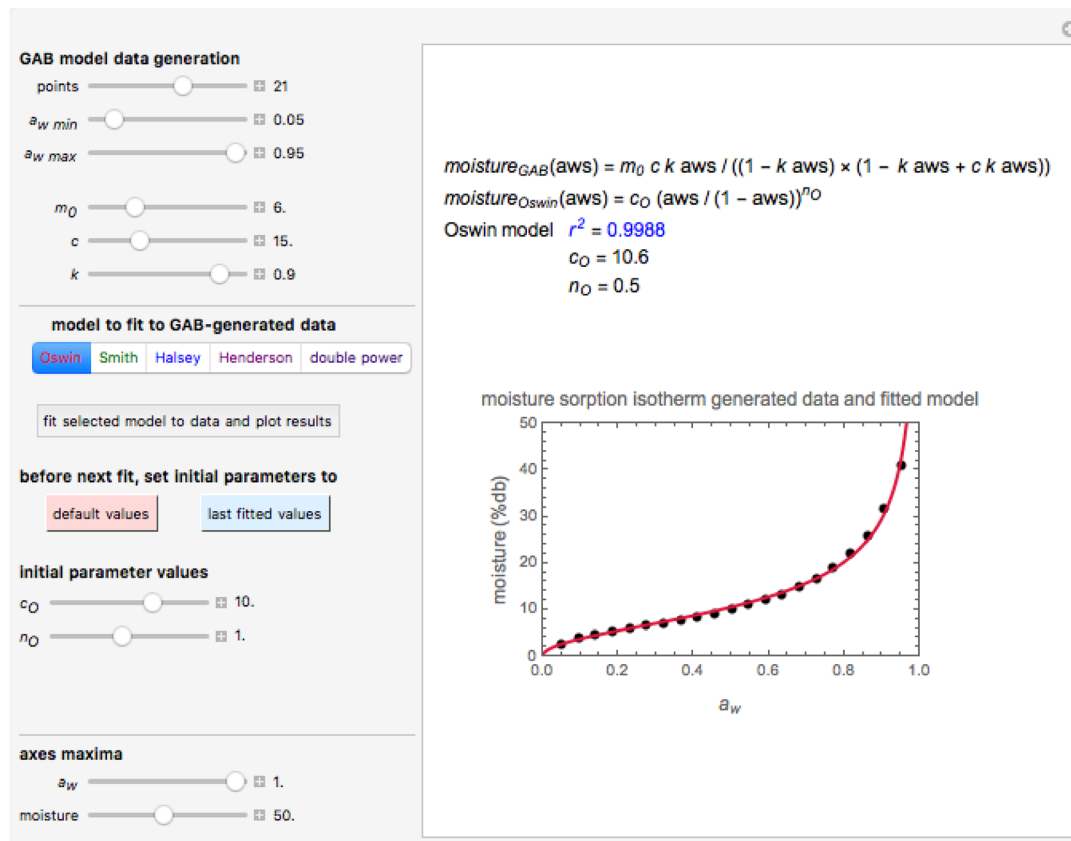## Comparison of Food Moisture Sorption Isotherm Equations

Fig. 3 Screen display of the interactive Wolfram Demonstration where generated GAB moisture sorption isotherms can be fitted with alternative models

using the BET, GAB or other models that have W_m in their equations, it has frequently found to be on the order of 200 m²/g, by far much larger than that obtained with nitrogen gas, which is usually one or two orders of magnitude smaller. Similar discrepancies have been amply reported in pharmaceutical and other non-food materials, e.g., [18]. At the same time, when nitrogen and argon (or krypton, or helium) have been used as adsorbents (in non-food materials), no such discrepancies have been observed.

To explain the discrepancy, one could claim that it is due to individual water molecules' small size, which enables them to penetrate and settle in smaller pores and cavities that the larger nitrogen molecules cannot, i.e., that the food matrix acts as a molecular sieve. Although not theoretically impossible, since the nitrogen molecule's projected area is only about 60% larger than that of a water molecule, this is an unlikely a correct explanation of differences of *one or two orders of magnitudes*, especially in the calculated specific surface areas *of nonporous foods*. In principle, this issue could be settled by comparing the specific surface area of foods determined with water vapor and with helium gas whose molecule's projected area is about 10% smaller than that of water. However, because of the extremely low boiling point of helium, reports on

such comparisons are very difficult to find in the literature and are unlikely to emerge any time soon. Comparisons made in non-food materials between the specific surface areas determined with helium and nitrogen whose molecules projected area is about twice as large showed no large or consistent differences [18, 32].

In addition to these three issues, had the BET/GAB water monolayer represented an actual physical surface, its value should have been temperature independent and the same when determined by different methods and calculated with different models.

In light of the above, it has been recognized that water vapor sorption by foods and hygroscopic biological materials in general is more akin to *chemical sorption* than to physical adsorption of an inert gase on a solid surface, from which the monolayer concept has originated. Yet, to save the analogy, it has been suggested that water vapor molecules interact with hydrophilic groups such as OH or NH, which in foods (and in other biological materials) are by far more abundant than the physical sites on which an inert gas molecules can settle. This description of the moisture sorption phenomenon is most probably correct. It might also explain the independence of food powders' specific surface area of their particle size when calculated from moisture sorption isotherms. However, there

are two issues with this explanation: One is that the measured specific surface area of microcrystalline cellulose significantly depends on its degree of crystallinity, which must have very little effect if any on the number of hydrophilic groups. Another is the huge difference between the water sorption capacity of amorphous and crystalline sugars, which offers an even more dramatic example that the number of hydrophilic groups alone is insufficient to explain the water sorption pattern. The second issue is that because the *degree of hydrophilicity* (the opposite of hydrophobicity) of sites on large molecules such proteins and starches most probably vary, perhaps almost continuously, there is no reason to believe in the existence of a unique moisture contents that marks a transition in their affinity to water vapor. Or alternatively, any supposition that there exists a unique point marking the saturation of all or a critical number of available hydrophilic sites would have to be supported by *independent physical evidence*.

BET/GAB Type Moisture Sorption Models Without an Assumed Monolayer

The water monolayer's existence issue can also be challenged from a different angle. In 1993, we have proposed the semi-empirical double power-law model having the form [20]:

$$m(a_W) = c_1 a_w^{n_1} + c_2 a_w^{n_2} \tag{17}$$

where, for sigmoid (Type II) isotherms, $n_1 < 1$ and $n_2 > 1$. [This model can and has successfully described Type III isotherms with $n_1 \geq 1$ and $n_2 > 1$, but this should not concern us here.]

Not surprisingly as already stated, having four adjustable parameters, its fit to experimental moisture sorption data has been comparable with and not infrequently slightly better than that of the three-parameter GAB model and of course the two two-parameter models. Since the "winning model" in such comparisons has not been consistently the same one even in the same food at different temperatures, one may legitimately suspect that accidental experimental scatter had also played a role.

The reason of proposing the double power-law model was certainly not to improve the fit at the expense of an added adjusted parameter as some have inferred, e.g., [3, 11]. The purpose of its introduction has been to demonstrate that one can model and attempt to explain the ubiquitous sigmoid shape of moisture sorption curves in foods and other hygroscopic materials *without assuming the water monolayer physical existence*. Equation 17 is a reflection of the alternative notion that, in contrast with an inert gas being adsorbed on a solid surface, moisture sorption by foods and other biological and non-biological materials is

governed by two juxtaposed processes: one with a scaling exponent smaller than one (n_1) and the other with a scaling exponent bigger than one (n_2) as shown in Fig. 1 (Type IIb). But before comparing the two concepts, let us first address the inflection point, a relevant issue concerning the nature of sigmoid curves and mathematical description of their shape.

The Inflection Point

The Double Power-Law Model

By definition, a sigmoid curve reverses it concavity direction at the inflection point where the function's second derivative equals zero. In the double power-law model (Eq. 17), the inflection point's water activity, $a_{W\ inflection}$, is the solution of $d^2m(a_W)/da_W^2 = 0$ equation, which happens to be analytic, i.e.

$$a_{W\ inflection} = \left[-\frac{(c_1\ (\ n_1-1)\ n_1)}{(c_2\ (\ n_2-1)\ n_2)} \right]^{\frac{1}{n_2-n_1}} \tag{18}$$

The corresponding moisture content $m(a_{W\ inflection})$ can be calculated inserting $a_{W\ inflection}$ into Eq. 17. Thus, according to the double power-law model, the actual inflection point's coordinates are determined by the particular combination of all four model's parameters, c_1, n_1, c_2 and n_2, none of which is indicative of a water monolayer's existence. The same can be said about the other non-BET/GAB models, except that their inflection point's location and corresponding moisture content are determined by a particular combination of their own parameters. Equation 18 permits parameter combinations that produce $a_{W\ inflection} > 1$, i.e., outside the physical water activity's range ($0 \leq a_W \leq 1$). This translates into a hypothetical but not totally unrealistic scenario where the two underlying sorption mechanisms, one with exponent scaling lower than one ($n_1 < 1$) and the other larger than one ($n_2 \geq 1$), produce a Type I (Langmuir) sorption isotherm at least in appearance, i.e., having downward concavity over the entire relevant a_W range. If so, then at least theoretically, observed downward concavity all the way by itself does not exclude the possibility that there still exist two (or more) parallel sorption mechanisms acting simultaneously. Thus, although the notion that the downward concavity of a Type I sorption isotherm indicates progressive coverage of the available sorption sites can be still theoretically correct, its validation cannot come from the curve's shape alone, unless a truly constant moisture level is clearly reached.

On the basis of the above, and we will bring additional reasons, one must conclude that the moisture sorption isotherm's shape alone *does not contain enough information* to establish the physical existence of a monolayer value and cannot be used to dismiss claims of its nonexistence. Similarly, although the inflection point's location can be

legitimately viewed as associated with the relative weights of two (or more) coexisting sorption mechanisms, it need not coincide with any presumed monolayer value. Or said differently, the inflection point's location has no special mechanistic significance beyond marking the water activity level at which the already operating sorption mechanism having the higher exponent scaling becomes predominant.

The GAB and BET Models

The GAB model of moisture sorption isotherms, as already stated, can be written in the form of Eq. 16 having three uncompounded parameters c_1, c_2 and c_3. In contrast with the unique solution of the double power-law model, Eq. 18's $d^2m(a_W)/da_W^2 = 0$, where $m(a_W)$ is defined by the GAB model, has *three* analytic solutions, one real and two complex. The GAB moisture sorption curve's actual inflection point's location is the real root of the equation, which, like the two complex roots, is a very cumbersome algebraic expression. Moreover, unlike in the double power-law model where all four parameters appear in the solution's algebraic expression (Eq. 18), in the GAB model c_1 is cancelled out in all three solutions, and only contains c_2 and c_3. [The cumbersome explicit real root's expression can be used to calculate the GAB isotherm's inflection points for any c_2 and c_3 pair directly. With Mathematica® (Wolfram Research, Champaign IL), the program used to generate the figures of this work; this can be also done with the FindRoot function applied to the second derivative of the original model equation, i.e., without writing the explicit algebraic solution.]

Notice that c_1 is the only term in the GAB model's equation that contains the monolayer value, W_m. In other words, the curve's inflection point's location is only determined by c_2 and c_3 and therefore has nothing to do with the monolayer value.

Also, the algebraic expression of the GAB moisture sorption curve's inflection point, $a_{W\ inflection}$, does not restrict its upper limit to 1.0, provided that $c_3 > 1$. However, it is highly doubtful that this observation has any practical implications in the GAB model's use.

Again, from a purely formalistic viewpoint, the BET equation is just a two-parameter model in the form of Eq. 5 characterized by c_1 and c_2, which is a special case of the GAB model where $c_3 = 1$. Either way, when $m(a_W)$ is described by the BET equation, the analytical solution of $d^2m(a_W)/da_W^2 = 0$ is only slightly less cumbersome than that of the GAB model. And, as expected, the BET model's $a_{W\ inflection}$ too is independent of c_1 and hence of the monolayer value. In contrast with the GAB model's inflection point, the BET's $a_{W\ inflection}$ must always be smaller than one, i.e., its location on the a_W-axis must be somewhere before the sorption curves rapid ascent to infinity as $a_W \rightarrow 1$.

Comparison of the Sorption Curves Generated with the Two Kinds of Models

Perhaps the main reason the double power-law model has not caught on is that it has four adjustable parameters while the GAB model only three. It therefore makes perfect sense to demand that a comparison between them should be made when they both have the same number of adjustable parameters. To resolve the number of adjustable parameters issue associated with Eq. 17 as a sorption model, let us examine the model's underlying concept when implemented in *three-parameter models*, i.e., having the same number of parameters as the GAB model.

To do that, consider the following. The GAB model as described by Eq. 16 can be rearranged and written in the form

$$m(a_W) = \frac{Aa_W}{(1 + c_2a_W)} + \frac{Ba_W}{(c_3 - a_W)} \tag{19}$$

where $A = c_1c_2/(1+c_2c_3)$ and $B = c_1/(1+c_2c_3)$. This presentation of the sorption isotherm equation in the form of a sum of two terms is very similar to the four-parameter model offered in [30]. They differ in that Eq. 19 is *mathematically identical* to the GAB model, i.e., they both have the same three parameters c_1, c_2 and c_3, albeit rearranged. [Actually, the starting point of the BET model derivation was the coexistence of two sorption regimes so here we go in reverse.] The first term in Eq. 19 is a function of a_W having an asymptotic value, $c_1/(1 + c_2c_3)$, and the second term a function of a_W that grows monotonically at an ever increasing pace, approaching infinity as $a_W \rightarrow c_3$, as shown schematically in Fig. 1 and marked as a Type IIa isotherm. Notice that here again, from a purely formalistic viewpoint, the BET equation is just a special case of the GAB model where $c_3 = 1$, i.e., the first term's asymptote is $c_1/(1 + c_2)$, and the second term approaches infinity as $a_W \rightarrow 1$. We can now consider the hypothesis that a sigmoid equilibrium moisture sorption isotherm is indeed governed by two such mechanisms: saturation of sorption sites (however defined) represented by the first term in Eq. 19, and condensation of water molecules on other water molecules, i.e., not on the solid surface itself, represented by the second term of the equation. The first mechanism, like in the BET and GAB models, implies the existence of an asymptotic or actual amount of absorbed water, which has been traditionally associated with a "water monolayer." The second component dominated by condensation has no such limit (and involves much less energy). According to the monolayer hypothesis, the second mechanism "takes over" when most or all the available sorption sites on the solid surface have already been occupied or interacted with.

The alternative scenario is that, *unlike in the adsorption of an inert gas on a solid surface*, there is no such a thing as a "water monolayer." In this case, the first component can rise

monotonically with the water activity, and it has no asymptotic level, while the second, which is marginal at low a_W levels, takes over at higher ones. Here are two examples of alternative *three-parameter models* that describe such a scenario:

A reduced three-parameter version of the double power-law model

$$m(a_W) = c(a_W^{n_1} + a_W^{n_2}) \qquad (20)$$

where $n_1 < 1$ and $n_2 \geq 1$.
and the hybrid model

$$m(a_W) = c_1 a_W^{n} + \frac{a_W}{c_2 - a_W} \qquad (21)$$

where $n < 1$ and $c_2 > 1$.

To avoid an experimental scatter issue, let us examine these two models' fit not to actual experimental moisture sorption data but to data generated with published GAB model parameters (Eq. 15) taken from [16]. We have chosen three major common food components, protein (casein), starch (potato starch) and cellulose and pea flour, presumably having all three types as components. The generated data sets, all for 25 °C, are fairly dense, each has 12 points excluding the origin (0,0), which cover the range of water activities from 0.06 to 0.94. [The lower end is slightly lower than in most food publications, which has been frequently 0.11 (obtained with a saturated LiCl solution).] All the shown water activities can be obtained with the saturated solutions of readily available salts, which are listed in numerous publications and on the Internet [e.g., http://manuals.decagon.com/Application Notes/13463_Temp Dependence of the Aw of Sat Salt Solutions_Print.pdf].

Eqs. 20's and 21's to the sorption data generated with the published GAB parameters is shown in Figs. 4, 5, 6 and 7. The calculated corresponding regression coefficients, r^2's, were rounded to the fourth digit after the decimal. As could be

expected from that Eqs. 20 and 21 are not mathematically identical to the GAB model equation, none of the fitted plots had a perfect fit ($r^2 = 1.0000$). But being in the range of 0.9995–0.9998 for the casein, 0.9999–0.9991 for the potato starch, 0.9981–0.9988 for the cellulose and 0.9981–0.9978 for the pea flour, they are all still very high as judged visually as well as by the statistical criterion.

Without exception, all the above listed regression coefficients are at least about as high as those calculated using the GAB model to fit experimental data, which almost invariably cover smaller water activities ranges. In practical terms, therefore, it means that within the water activities range examined, both Eqs. 20 and 21 could be used interchangeably between them and also with the GAB model (Eq. 16). This is despite not having an asymptotic term in their equations and regardless of the sorption curve's steepness at the very high water activities, which is represented by their second terms. Also worth mentioning is that for the potato starch and pea flour, Eq. 20 had a very slightly higher r^2 than Eq. 21, while Eq. 21 had a very slightly higher r^2 than Eq. 20 for the casein and cellulose. In other words, it seems that neither model was consistently superior nor inferior as far as the fit is concerned.

The BET Plot: The Monolayer and Specific Surface Area

Historically, food's water monolayer value was determined from its linearized BET moisture sorption isotherm in the water activity range of about 0.1 to 0.5, using Eq. 14 with $x = a_W$ for the calculation. With the monolayer value determined in this manner, and the known effective area of the water molecule, a food's specific area could be calculated and reported. For the GAB and related models, including the BET, the monolayer value can also be determined by regression using the untransformed moisture sorption data. An
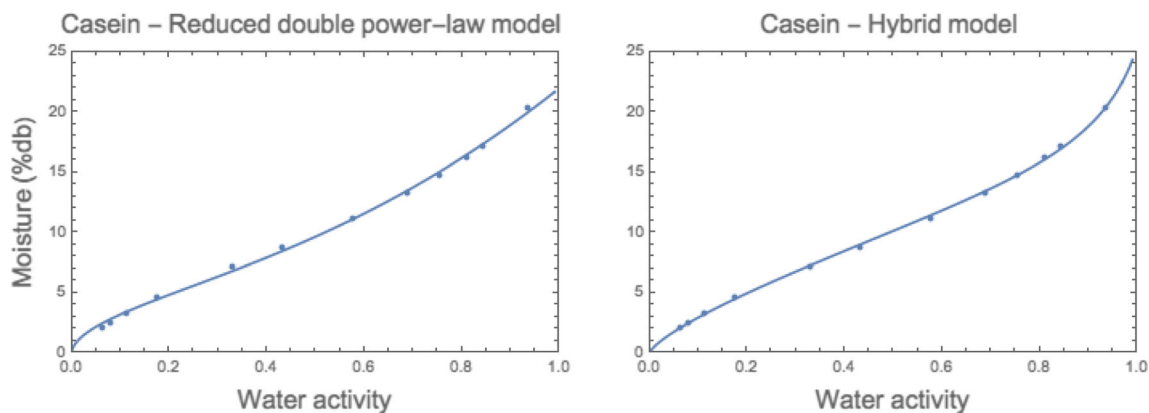
Fig. 4 Equilibrium moisture sorption data of casein generated with its published GAB equation parameters [16] and fitted with two alternative three-parameter models; Eq. 20 (left) and Eq. 21 (right). These two models represent two hypothetical underlying sorption mechanisms that have no water monolayer in their formulation
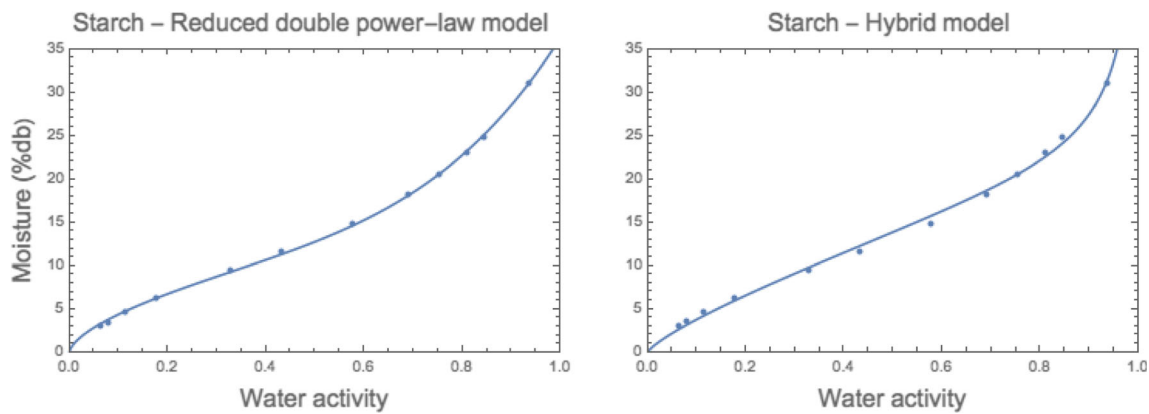
Fig. 5 Equilibrium moisture sorption data of potato starch generated with its published GAB equation parameters [16] and fitted with two alternative three-parameter models; Eq. 20 (left) and Eq. 21 (right).

These two models represent two hypothetical underlying sorption mechanisms that have no water monolayer in their formulation

interesting question that arises is what will happen if we apply Eq. 14 to sorption data generated with a model equation that a priori *has no monolayer value* in its formulation. Figure 8 shows such data plots, i.e., $1/(m(a_w)(1/a_w - 1))$ vs. a_w data sets where $m(a_w)$ was generated with the reduced double power-law model (Eq. 20). The models' coefficients are those used to create the left plots in Figs. 4, 5, 6 and 7. As expected, the four data plots shown in the figure appear to be lying on a straight line at least visually. Had these points been experimental and subjected to linear regression, the resulting r^2 would certainly be high, tempting one to consider the plot's linearity as the BET model affirmation, and use the resulting W_m's to calculate the four foods' specific surface areas. With experimental scatter added, the situation would be even murkier and the reality of the calculated specific surface area even more difficult to establish. Or said differently, the apparent linearity of the BET plot by itself does not confirm the water monolayer's existence, which if true must also come from independent physical evidence and not from the shape of the moisture sorption isotherm alone.

Can There Be More Than Two Moisture Sorption Mechanisms?

From a purely formalistic viewpoint, a sigmoid moisture sorption curve of the kind ubiquitous in foods can be generated with any number of underlying sorption mechanisms. Two hypothetical examples are given in Fig. 9. The moisture sorption isotherm in both plots (solid curve) is that of wheat flour also shown in Fig. 1, but the three underlying dotted curves were produced with parameters obtained by fitting the same data with two different models each having *three* underlying sorption mechanisms and not two. These two models are expanded versions of the double power-law model (Eq. 17) in the form

$$m(a_W) = c_1 a_w{}^{n_1} + c_2 a_w{}^{n_2} + c_3 a_w{}^{n_3} \tag{22}$$

i.e., neither having a monolayer term in their mathematical construction. The two plots differ in that in the one on the left $n_1 < n_2 < 1 < n_3$ (marked LLH) while that on the right $n_1 < 1 < n_2 < n_3$ (marked LHH). In other words, in the first there is one
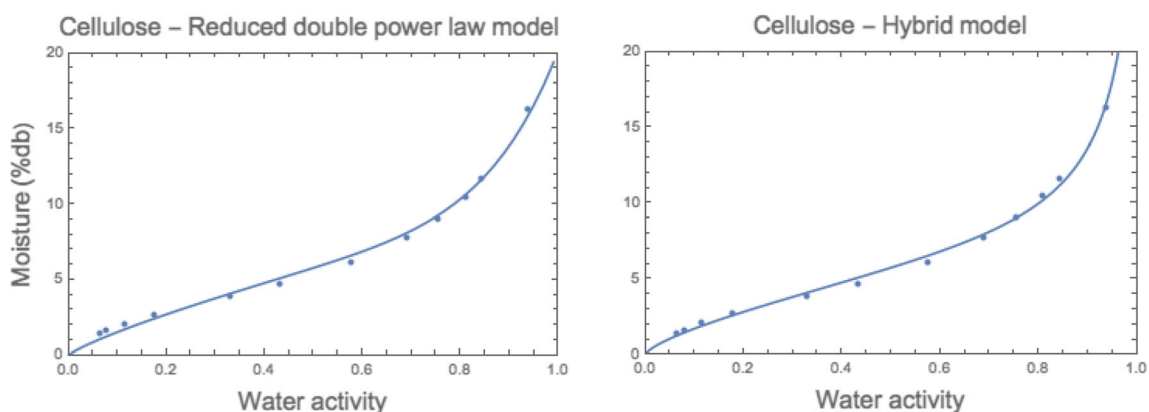

Fig. 6 Equilibrium moisture sorption data of cellulose generated with its published GAB equation parameters [16] and fitted with two alternative three-parameter models; Eq. 20 (left) and Eq. 21 (right). These two

models represent two hypothetical underlying sorption mechanisms that have no water monolayer in their formulation
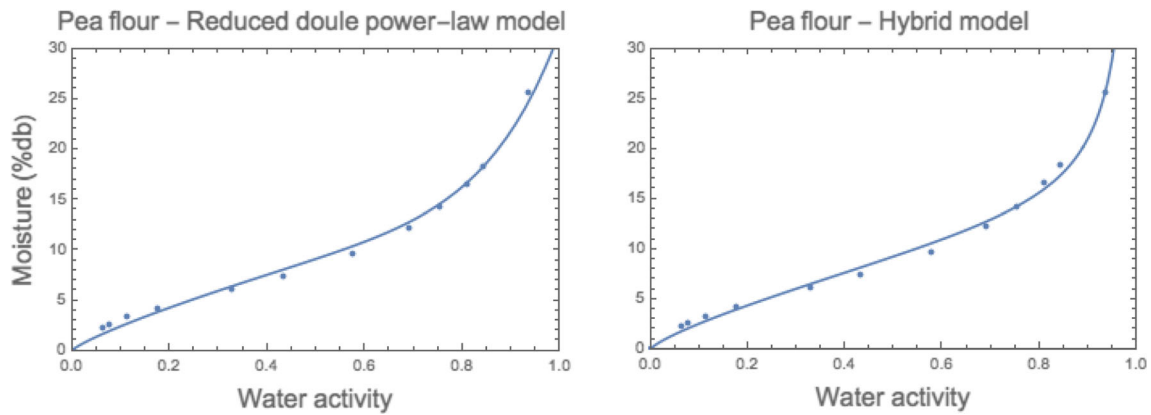
Fig. 7 Equilibrium moisture sorption data of pea flour generated with its published GAB equation parameters [16] and fitted with two alternative three-parameter models; Eq. 20 (left) and Eq. 21 (right). These two models represent two hypothetical underlying sorption mechanisms that have no water monolayer in their formulation

mechanism with an exponent scaling larger than one and two mechanisms with an exponent scaling lower than one, while in the second there are two mechanisms with an exponent scaling larger than one and only one having an exponent scaling smaller than one—see the underlying dotted curves' concavity direction. These plots are by no means unique. In principle there is no limit on the number of underlying curves that can be constructed with models of Eq. 22's type and the number of their terms. The same can be said on alternative "hybrid-type" models (see Eq. 21) and the number and form of their terms.

Showing Fig. 9 is not a suggestion that there actually exist more than two underlying sorption mechanisms. This might but need not be true. The figure sole purpose is to demonstrate
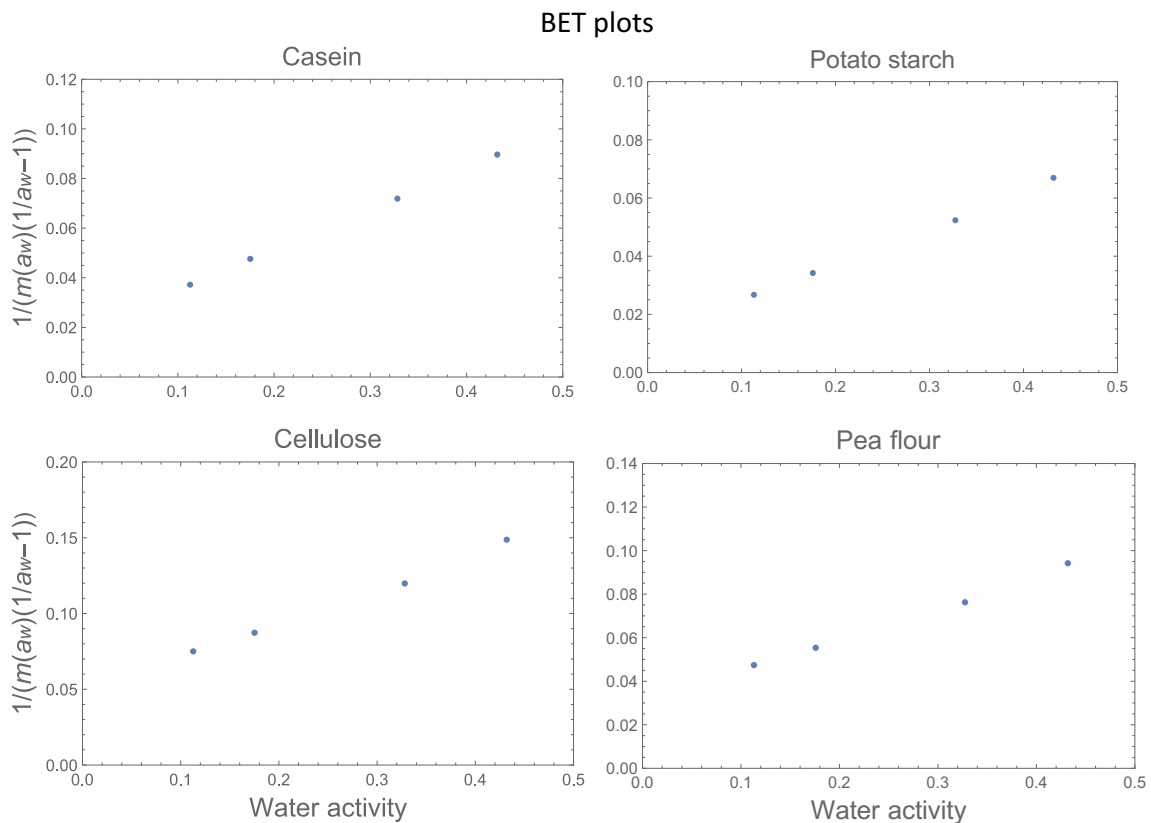

Fig. 8 Linearized BET plots generated for the three-parameter double power-law model (Eq. 20) as the sorption model. Notice that had the points been actual experimental data, one would be tempted to calculate corresponding monolayer values despite that the model used to generate them has none

Fig. 9 The sigmoid equilibrium moisture sorption isotherm of wheat flour, constructed with two different combinations of three hypothetical underlying moisture sorption mechanisms, left and right, using Eq. 22 as a model. Notice that the two shown sorption curves are indistinguishable from those in Fig. 1, indicating that the curve's shape alone does not contain enough information to identify even the *number* of underlying sorption mechanisms
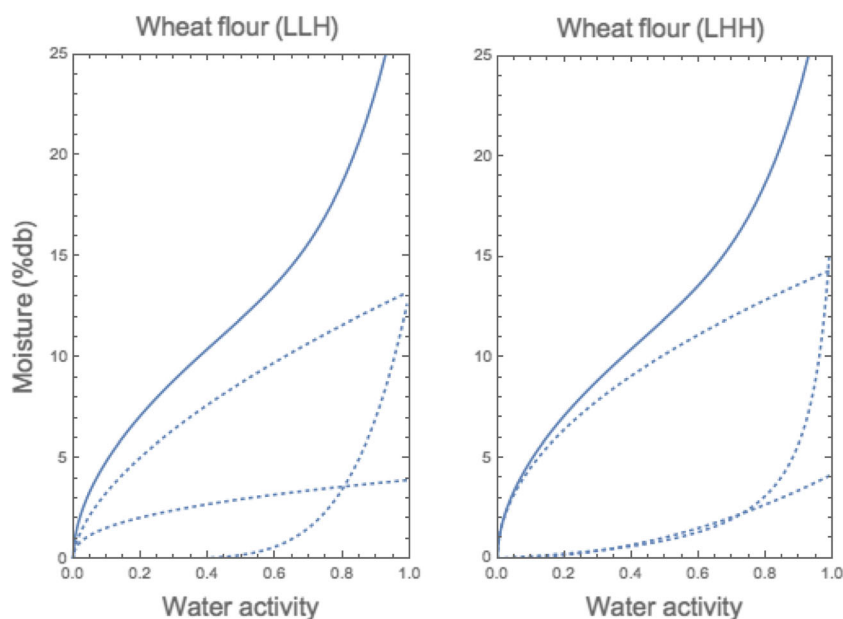
that the shape of a moisture sorption isotherm alone is insufficient to identify the number and character of the underlying sorption mechanisms, let alone quantify their relative roles. This is in contrast with the BET equation when applied to inert gases adsorption on solid surfaces, where the model's confirmation comes not from its fit to experimental data but from comparison of the specific surface area when determined with inert gases of two or more molecular species.

Conclusions

Despite being almost universally taken for granted in and food science research and education, the water monolayer existence is still unproven and perhaps should be treated as a conjecture rather than a hypothesis. In contrast with inert gases adsorption, where there is agreement between specific surface areas determined with different gases and the finer a powder the larger its specific surface area is, the available physical evidence does not support the water monolayer reality. This review lends support to the notion that the moisture sorption isotherm's shape alone does not contain enough information to uniquely identify and quantify the underlying sorption mechanisms. The simulations and regression analysis clearly demonstrate that models constructed without assuming the monolayer existence render sorption curves that for all practical purposes are indistinguishable from those described by the BET/GAB type models. This returns the burden of proof of the monolayer concept utility to those who attempt to explain and predict food stability or instability on the basis on its presumed existence. Although the role of temperature has not been specifically addressed in this work, the mathematical analysis also suggests that no point on the

equilibrium moisture sorption curve, including the inflection point, marks a physical phase transition.

At this time, the notion that there exist at least two principal sorption mechanisms with exponent scaling smaller and larger than one is still an unproven hypothesis too and for the very same arguments used to criticize the monolayer concept. Before being generally accepted, the proposed alternative concept ought to be validated by independent physical evidence, because good fit alone is insufficient. But, unlike the BET/GAB-type models when applied to moisture adsorption foods, the proposed alternative is at least consistent with the observed physical characteristics of the moisture sorption phenomenon. Therefore, the original introduction of the double power-law model [20], and of its two reduced three-parameter versions in this work, should not be viewed as an exercise in curve fitting, but as an attempt to demonstrate that the nature of the moisture sorption phenomenon in foods can be captured without invoking the analogy to inert gases adsorption that cannot be sustained.

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