Augmented Brunauer–Emmett–Teller Equation for Water Adsorption on Soils

Chao Zhang and Ning Lu*

An augmented Brunauer–Emmett–Teller (BET) equation was developed for describing water adsorption on soils, overcoming the limitation of the original BET equation for describing only isotherms of materials with a homogeneous adsorption surface. The different physicochemical mechanisms underlying water adsorption in soils are synthesized, leading to a unique adsorption sequence dictated by two distinguishable free energy levels. The higher adsorption free energy level reflects the internal (intra-crystalline) surface adsorption, whereas the lower adsorption free energy level reflects the external (particle) surface adsorption. This adsorption energy disparity is provided by the interlamellar energy barrier of van der Waals and electrostatic attractive forces. Consequently, an augmented BET equation was formulated as a combination of the individual BET equations for the internal (intra-crystalline) surface adsorption and external (particle) surface adsorption. The augmented BET equation demonstrates excellent performance in representing measured water adsorption isotherms of a wide suite of silty and clayey soils, validating its applicability. The augmented BET equation excellently predicts the expected dominance of the external particle surface adsorption of the non-polar N adsorption on clay soils, illustrating its ability in separating external and internal surface adsorption. Additionally, the specific surface area estimated by the augmented BET equation matches well the estimation by two independent methods, further confirming the validity of the augmented BET equation.

The sorption isotherm is a material’s constitutive relationship between the mass of sorbate per unit mass of sorbent and the ambient relative humidity or vapor pressure under isothermal conditions. Thermodynamically, the isotherm for water adsorption on soils quantifies the energy magnitude of the soil–water interaction, therefore it is a vital constitutive relationship governing a wide array of fundamental behaviors of soils such as the swelling potential (e.g., Likos, 2008), soil water density (Zhang and Lu, 2018a, 2018b), the phase transition of soil water (Lu and Zhang, 2019), and hydraulic conductivity (e.g., Or and Tuller, 1999). In practice, the sorption isotherm can be accurately measured by commercial equipment (e.g., Likos et al., 2011) and thus is commonly utilized to determine fundamental soil properties such as the specific surface area (SSA) and cation exchange capacity (e.g., Akin and Likos, 2016; Khorshidi et al., 2017; Khorshidi and Lu, 2017). Various empirical or physical equations have been developed to quantify sorption isotherms in various scientific disciplines. Among them, the Freundlich equation (Freundlich and Mäkelä, 1909) was the first mathematical model but purely empirical; the Langmuir equation (Langmuir, 1918) was the first physics-based equation but limited to an energetically homogeneous surface and monolayer of sorbate. The Brunauer–Emmet–Teller (BET) equation (Brunauer et al., 1938) overcomes the limitation to a monolayer of sorbate and currently is a commonly used model to describe the multilayer adsorption of gas molecules on a sorbent (Brunauer et al., 1938). For water adsorption, the BET equation can be written as
This equation can be reorganized in a linear form between RH/\([w(1-RH)]\) and RH:

$$\frac{RH}{w(1-RH)} = \frac{c-1}{w_m c} RH + \frac{1}{w_m c^2}$$

where \(w\) is the gravimetric water content \((g \cdot g^{-1})\), RH is the relative humidity, \(w_m\) is the monolayer water content \((g \cdot g^{-1})\), and \(c\) is a constant related to the enthalpy of adsorption. Therefore, for any material whose adsorption follows the BET theory, the isotherm data should exhibit a linear relationship in the RH/\([w(1-RH)]\) vs. RH plot space.

One main tacit assumption involved in the BET equation is the energetically homogeneous adsorption surface, which is not valid for some clayey soils, particularly for swelling clays. For example, the BET equation can well represent the isotherm data of non-swelling soils like Georgia kaolinite (Fig. 1a) but not for that of a swelling soils like Wyoming bentonite, as qualitatively illustrated in Fig. 1. The probable reason is that the adsorption energy on the internal surface is quite different from that on the external surface due to the additional energy input to overcome the energy barrier provided by the attraction of the van der Waals and electrostatic forces between lamella (e.g., Laird et al., 1995; Lu and Khoshidi, 2015; Zhang and Lu, 2018b). Consequently, the linear BET plot breaks down for swelling soils, as shown in the RH/\([w(1-RH)]\) vs. RH plot of the isotherm data for Wyoming bentonite in Fig. 1b.

Despite its inability to model swelling soils (Fig. 1b), the BET equation has been widely selected as a common approach to determine the SSA for both non-swelling and swelling soils (e.g., Mooney et al., 1952; Quirk, 1955; Yukselen and Kaya, 2006; Akin and Likos, 2016). According to Eq. [2], the measured sorption isotherm can be plotted in the space of RH/\([w(1-RH)]\) vs. RH, and the values of \(w_m\) and \(c\) can be estimated from the slope of \((c-1)/(cw_m)\) and intercept of \(1/(cw_m)\). The BET method requires multiple sorption isotherm data points for a linear fitting and therefore is also referred to as the multiple point method.

In contrast, single point methods previously developed (e.g., Quirk, 1955; Puri and Murari, 1964; Newman, 1983; Arthur et al., 2013) rely on the determination of the relative humidity point at which the adsorbed water molecules are assumed to reach monolayer coverage.

The prerequisite for the existence of a universal monolayer coverage relative humidity is that the free energy at the monolayer coverage is a constant regardless of mineral type. However, such a prerequisite is subjective due to the fact that different mineral types exhibit distinct molecular structures and surface properties and thereby distinct soil–water interaction energies (e.g., Zhang et al., 2016; Zhang and Lu, 2018a, 2018b). Based on different soil datasets, researchers have found remarkably divergent monolayer coverage relative humidity values, e.g., RH = 20% (Quirk, 1955; Arthur et al., 2013), RH = 53% (Newman, 1983), and RH = 53% (Puri and Murari, 1964). Khoshidi et al. (2017) developed a procedure to determine the monolayer coverage relative humidity based on the cross points in soil moisture capacity (SMC) between adsorption and desorption isotherms (referred as the SMC method), revealing that the monolayer coverage relative humidity varies with soil type but can be identified by the cross point in the SMC. The SMC is the derivative of the isotherm with respect to relative humidity and thus is highly sensitive to the accuracy of the isotherm data. As such, the SMC method is subject to uncertainty in determining the cross point, especially for relatively low swelling soils, because the difference between adsorbed and desorbed SMCs could be insignificant.

In general, the SSA can be estimated from the monolayer water content \(w_m\) as (e.g., Akin and Likos, 2016; Khoshidi et al., 2017)

$$\text{SSA} = \frac{w_m N_A A_m}{M_w}$$

where \(N_A\) is Avogadro’s number, i.e., 6.02 \(\times\) \(10^{23}\) mol\(^{-1}\); \(A_m\) is the area occupied by one water molecule, which depends on soil water density (Zhang and Lu, 2018b), and is commonly assumed to be a constant of 10.8 \(\times\) \(10^{-20}\) m\(^2\) for simplicity; \(M_w\) is the molar mass of water, i.e., 18.02 g mol\(^{-1}\); \(n\) is an empirical coefficient that is subjected to great uncertainties because it highly depends on the expansibility of the soil.

![Fig. 1. Fitting the Brunauer–Emmett–Teller (BET) equation to adsorption isotherm data (from Khoshidi et al., 2017) of end member clay minerals: (a) a non-swelling soil, Georgia kaolinite, showing linear behavior, and (b) a swelling soil, Wyoming bentonite, showing nonlinear behavior; RH is relative humidity and \(w\) is the gravimetric water content.](image-url)
The physical rationale behind involving parameter $n$ is that for swelling soils, water molecules are able to penetrate into the interlayer space, and the monolayer water will be sandwiched by adjacent internal surfaces; thereby, the internal surface area needs to be estimated using double monolayer water content. In practice, the value of $n$ is suggested to be 1 for non-swelling soils dominated by external surface adsorption and 2 for swelling soils dominated by internal surface adsorption (e.g., Khorshidi et al., 2017). However, in reality, the water adsorption on soils is not solely due to internal surface adsorption but is concurrently due to external surface adsorption (e.g., Mooney et al., 1952). As such, the concurrent internal and external surface adsorption in swelling soils cannot be properly accounted for by the value of $n$.

In this study, a mathematical isotherm equation was developed for water adsorption on soils by modifying the BET equation. The objectives for the current study were threefold: (i) to develop an isotherm equation for both swelling and non-swelling soils; (ii) to separating water adsorption on the internal and external surfaces by synthesizing physicochemical mechanisms; and (iii) to provide a universal approach to estimate the SSA of soils from water adsorption isotherm data.

**Adsorption Energy Heterogeneity and Sequence**

**External and Internal Surface Adsorption**

The spatial heterogeneity of adsorption energy on soil is the main reason why the BET equation cannot quantitatively describe water adsorption on many clayey soils. Physically, this spatial energy heterogeneity stems from the distinct adsorption energy levels of water adsorption between internal and external surfaces in clayey soils. Here, the external surface adsorption refers to the adsorption on the external particle surface or the hydration on cations retained on the external particle surface, whereas the internal surface adsorption is defined as the adsorption on the interlamellar surface or the hydration on cations retained on the interlamellar surface. Here the physicochemical forces underlying the external and internal surface adsorption are discussed to shed light on why and how the adsorption energy deviates between the internal and external surfaces.

The external surface adsorption is driven by the physicochemical mechanisms of multilayer adsorption, surface hydration, and cation hydration as illustrated in Fig. 2. The intermolecular forces underlying these physicochemical mechanisms and the corresponding energy levels are also summarized in Fig. 2. The magnitude of free energy change varies as $-10.8 \text{ kJ mol}^{-1}$ for multilayer adsorption, $-12.5$ to $-52.3 \text{ kJ mol}^{-1}$ for surface hydration (e.g., Tunega et al., 2004; Wang et al., 2006; Zhang et al., 2017), and $-250$ to $-1500 \text{ kJ mol}^{-1}$ for cation hydration (e.g., Marcus, 1991; Salles et al., 2007). These free energy change levels dictate that, on wetting, the water molecules are first attracted to the cation retained on the surface, then surface hydroxyls and the mineral crystals; the external surface adsorption energy is bounded by the cation hydration energy of $-1500 \text{ kJ mol}^{-1}$.

The internal surface adsorption, in contrast, is mainly determined by the interlamellar cation hydration, as shown in Fig. 2. In an oven-dry state, the clay lamellae are closely bonded to each other by attraction of the intense van der Waals and electrostatic forces between lamella. As such, the interlamellar space is closed and inaccessible to water molecules. Upon wetting, part of hydration energy needs to be consumed by water molecules to overcome the van der Waals and electrostatic attractive forces between the adjacent lamellae (e.g., Laird et al., 1995; Lu and Khorshidi, 2015). As a result, the cation hydration energy is shifted to higher or less negative energy levels of $-10$ to $-48 \text{ kJ mol}^{-1}$ (e.g., Salles et al., 2007). Therefore, the internal surface adsorption energy is bounded by the lower bound of $-48 \text{ kJ mol}^{-1}$, which is much higher or less negative than that of the external surface adsorption energy ($-1500 \text{ kJ mol}^{-1}$).

![Fig. 2. Physicochemical mechanisms related to external surface (left column) and internal surface (right column) adsorption of water on soils and corresponding free energy change levels and matric potential range (modified from Zhang and Lu, 2018b).](image-url)
**Adsorption Sequence**

As discussed above, the internal and external surface adsorption exhibit distinct energy levels. This difference in energy levels dictates that, on wetting or adsorption, the initiation of the internal surface adsorption, if any, always occurs later than that of the external surface adsorption. As such, the water adsorption on clays soils can be decomposed into two hydration stages, as demonstrated in Fig. 3 through two representative end-members of clay minerals: the 1:1 (one tetrahedral to one octahedral crystalline structure) clay mineral of Georgia kaolinite and the 2:1 (two tetrahedral to one octahedral crystalline structure) clay mineral of Wyoming bentonite. Georgia kaolinite represents the dominance of the external surface adsorption, whereas Wyoming bentonite represents the dominance of the interlamellar space. For Georgia kaolinite at the oven-dry stage, the exchangeable cations are mostly strongly attached to the external surface, as illustrated in Fig. 4a. In contrast, for Wyoming bentonite, both the external and internal surfaces have exchangeable cations, as illustrated in Fig. 4b.

Because of the disparity in the adsorption energy levels between the external and internal surfaces, a unique two-stage hydration sequence can be applied universally to the adsorption process in all soils, as follows.

**The First Hydration Stage:**

**External Surface Adsorption**

As illustrated in Fig. 4, under very dry conditions, e.g., RH < ~0.1 to 0.2, the adsorbed water molecules prevail on the external surface and are tightly bonded to exchangeable cations for both Georgia kaolinite and Wyoming bentonite. At such low RH, the water molecules are still not able to penetrate into the interlamellar space of Wyoming bentonite, and the layer spacing of Wyoming bentonite remains unchanged and around 9 Å. Therefore, at this stage, water adsorption is fully controlled by external surface adsorption for both Georgia kaolinite and Wyoming bentonite. The existence of this stage has been confirmed by some previous experimental observations (e.g., Mooney et al., 1952; Cases et al., 1992; Bérend, 1995; Salles et al., 2009).

**The Second Hydration Stage:**

**Concurrent External and Internal Surface Adsorption**

As RH increases, more and more water molecules will be adsorbed to the external surfaces of both Georgia kaolinite and Wyoming bentonite, as illustrated in Fig. 4. For Wyoming bentonite, the strong hydration forces provided by the interlamellar cations will allow the water molecules to overcome the energy barrier of the van der Waals attraction between lamellae. Thereby, the interlamellar space of Wyoming bentonite will expand, as shown in Fig. 4b, and the layer spacing can increased to >12 Å (e.g., Sposito and Prost, 1982; Hensen and Smit, 2002; Tambach et al., 2006), indicating the initiation of internal surface adsorption. In contrast, because most of the exchangeable cations reside on the external surfaces of Georgia kaolinite, and there is not enough driving force to open its interlamellar space, water adsorption on Georgia kaolinite remains dominated by external surface adsorption.

**Augmented BET Equation**

**Mathematical Formulation**

The universal adsorption sequence described above suggests that water adsorption on clayey soils can be interpreted as two independent physical processes, i.e., one with higher adsorption free energy (internal surface hydration) and the other with lower adsorption free energy (external surface hydration). As such, following the local thermodynamic equilibrium principle, i.e., the same relative humidity between the external and internal surfaces for a given total water content, the total adsorbed water content can be decomposed into the water adsorbed on the internal surface and that absorbed on the external surfaces:

\[
w(RH) = w_{\text{int}}(RH) + w_{\text{ext}}(RH)
\]  

where \(w_{\text{int}}\) is the gravimetric water content adsorbed on the internal surface (g g\(^{-1}\)) and \(w_{\text{ext}}\) is the gravimetric water content adsorbed on the external surface (g g\(^{-1}\)). Assuming that water adsorption on the external and internal surfaces follows the BET equation individually, the adsorbed water on the external and internal surfaces can be described as
where \( w_{\text{m-ext}} \) and \( w_{\text{m-int}} \) are the monolayer water contents adsorbed on the external and internal surfaces, respectively (g g\(^{-1}\)); \( c_{\text{ext}} \) and \( c_{\text{int}} \) are constants related to the enthalpy of adsorption on external and internal surfaces, respectively; and RH\(_0\) is the relative humidity point initiating adsorption on the internal surface.

The augmented BET equation can then be formulated by substituting Eq. [5–6] into Eq. [4]:

\[
w = \frac{w_{\text{m-ext}} c_{\text{ext}} \text{RH}}{(1 - \text{RH})(1 - RH + c_{\text{ext}}RH)}
\]

\[
w_{\text{int}} = \frac{w_{\text{m-int}} c_{\text{int}} \text{RH}_{0}}{[1 - (RH - RH_{0})][1 - (RH - RH_{0}) + c_{\text{int}}(RH - RH_{0})]}
\]

The total isotherm equation is a superposition of the isotherm equations for water adsorption on the external and internal surfaces. In the first hydration stage (RH < RH\(_{0}\)), all water adsorption is solely due to water adsorption on the external surface, whereas, in the second hydration stage (RH \(\geq\) RH\(_{0}\)), water adsorption on the internal surface also contributes to the total water adsorption.

**Fitting Isotherm Data**

To validate the augmented BET Eq. [7], extensive isotherm data from a variety of soils were used. A key issue in interpreting the isotherms of soil is the unambiguous determination of the upper limit of the RH for the isotherm data. In the high RH range (e.g., for most soil, RH > 50%), capillary condensation will participate in retaining water molecules on the soil matrix (McQueen and Miller, 1974; Lu and Likos, 2004; Lu, 2016), suggesting that the BET equation for pure surface adsorption will not hold beyond a certain RH value. The onset point of capillary condensation varies with soil mineralogy and pore topography, depending on soil type. Here, we adopted a theoretical way to determine the onset point of capillary condensation based on the local \( c \) value. The local \( c \) values at a certain RH are determined by fitting the five adjacent isotherm data points around a given RH. As such, the variation of the local \( c \) values with RH is attainable. Generally, this variation follows a unique trend and is illustrated in Fig. 6, showing consistence with the observation by Pomonis et al. (2004). For an RH value between 21 and 65%, the local \( c \) value switches sharply from positive values to negative values. This switch indicates the
breakdown of the BET equation, signifying the end of pure surface adsorption and accordingly the onset of capillary condensation in the interparticle corners and particle surfaces (e.g., Or and Tuller, 1999). The RH value at this switch is identified as the RH at the end of pure surface adsorption (RH_e). To ensure the accuracy of SSA estimation, only the isotherm data points of pure surface adsorption, i.e., RH < RH_e, are used to fit the augmented BET equation in the following analysis.

The proposed BET equation (Eq. [7]) involves five unknown parameters, viz., the monolayer water contents adsorbed on the external surface \( w_{m-ext} \) and the internal surface \( w_{m-int} \), the enthalpy of adsorption on the external surface \( c_{ext} \) and the internal surface \( c_{int} \), and the RH where the internal surface adsorption initiates (RH_0), which can be determined by best fits to the measured isotherm data. As indicated in Fig. 5 and Eq. [7], the augmented BET equation is a highly nonlinear function and cannot be reorganized into a linear form like the original BET (Eq. [2]), suggesting that a robust nonlinear fitting is required to determine the unknown parameters. In this study, a nonlinear least-squares algorithm was implemented in MATLAB (The MathWorks, 1998) and used to achieve the values of the physical parameters for best fits. To ensure the convergence of the fitting, initial guesses of the parameters pertinent to the external adsorption isotherm, i.e., \( w_{m-ext} \) and \( c_{ext} \), were first obtained by fitting the isotherm data with only the external BET equation for RH values <RH_e/3.

### Assessment of Augmented Equation

#### Experimental Dataset

A suite of 25 silty and clayey soils was selected to assess the performance of the augmented BET equation, as summarized in Table 1. The selected soil dataset covers a wide range of geotechnical properties, i.e., for the liquid limit (ASTM, 2010) from 12 to 485, for the plastic limit (ASTM, 2010) from 4 to 353, and for the plasticity index (ASTM, 2010) from 4 to 132. A soil’s plasticity index is directly related to its swelling ability or expansibility; qualitatively, the higher the plasticity index, the more a soil can swell in volume on wetting. The soil dataset includes water adsorption isotherms, ethylene glycol monomethyl ether (EGME) based SSA values, and N₂ adsorption isotherms. The water adsorption isotherms are available for all the selected soils and were taken from Akin and Likos (2014) and Khorshidi et al. (2017). The EGME-based SSA values for all the selected soils are from Akin and Likos (2014). The N₂ adsorption isotherms were measured with a Micromeritics ASAP 2000 analyzer for Georgia kaolinite and Wyoming bentonite.

### Water Adsorption Isotherm

As demonstrated through a variety of soils, the augmented BET equation can invariably well represent the adsorption isotherms of the selected 25 soils. The parameters obtained from...
the best fits are summarized in Table 2. The monolayer water content on the internal surface \( (w_{\text{m-int}}) \) varies significantly with soil type, i.e., from 0.000 to 0.076 g g\(^{-1}\). Generally, swelling soils (high plasticity index) tend to have higher \( w_{\text{m-int}} \), suggesting that internal surface adsorption is the main source responsible for the soil’s expansibility. In contrast, the monolayer water content on the external surface \( (w_{\text{m-ext}}) \) varies relatively little with soil type, i.e., 0.004 to 0.020.

The predicted RH when the internal surface adsorption initiates (\( \text{RH}_0 \)) varies from 0.01 to 0.21. The \( \text{RH}_0 \) value shows a strong dependence on the cation type, i.e., 0.01 for Ca-rich bentonite (Denver bentonite), 0.03 for Ca-bentonite, 0.03 for Mg-bentonite, 0.11 for K-bentonite, and 0.21 for Na-rich bentonite (Wyoming bentonite). This dependence can be explained by the dependence of the hydration energy on cation type; the higher the hydration energy, the higher the \( \text{RH}_0 \). For example, the energy of water hydrated on Na\(^+\) is lower than that on Mg\(^{2+}\), Ca\(^{2+}\), and K\(^+\) (e.g., Israelachvili, 2011; Khorshidi et al., 2016). It is anticipated that the lower hydration energy provided by the interlamellar Na cation makes it more difficult for the water molecules to overcome the energy barrier of the van der Waals and electrostatic forces between clay lamella. As such, it will be harder for water molecules to penetrate into the interlamellar space of Na-rich bentonite (Wyoming bentonite), leading to a higher \( \text{RH}_0 \) value.

The predicted relative humidity at the end of the pure surface adsorption \( \text{RH}_e \) varies from 0.21 to 0.65 with soil type, shown in Table 2. The transition of adsorption and capillarity is not a point but a zone, with a lower bound defined by the onset of capillarity and an upper bound defined by the complete decay of adsorption. The predicted \( \text{RH}_e \) value denotes the onset of capillarity.

Table 2. Fitted parameters for the augmented Brunauer–Emmett–Teller (BET) equation (Eq. [7]); \( w_{\text{m-ext}} \) and \( w_{\text{m-int}} \) are the monolayer contents adsorbed on the external and internal surfaces, respectively; \( \xi_{\text{ext}} \) and \( \xi_{\text{int}} \) are the constants related to the enthalpy of adsorption on external and internal surfaces, respectively; and \( \text{RH}_0 \), \( \text{RH}_e \), \( \text{RH}_{\text{m-ext}} \), and \( \text{RH}_{\text{m-int}} \) are the relative humidity values where the pure surface adsorption ends, the water content adsorbed on the external surface reaches the monolayer coverage, and the water content adsorbed on the internal surface reaches the monolayer coverage.

<table>
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<tr>
<th>Soil</th>
<th>Sorbate</th>
<th>( w_{\text{m-ext}} )</th>
<th>( w_{\text{m-int}} )</th>
<th>( \xi_{\text{ext}} )</th>
<th>( \xi_{\text{int}} )</th>
<th>( \text{RH}_0 )</th>
<th>( \text{RH}_e )</th>
<th>( \text{RH}_{\text{m-ext}} )</th>
<th>( \text{RH}_{\text{m-int}} )</th>
<th>( R^2 )</th>
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<td>0.99</td>
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<td>0.000</td>
<td>3.4</td>
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<td>0.35</td>
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<tr>
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<td>0.000</td>
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<td>0.03</td>
<td>0.23</td>
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<td>0.11</td>
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<td>0.12</td>
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† For water adsorption (g/g) and N\(_2\) adsorption (cm\(^3\)/g).
‡ N/A, not applicable.
and thus can be treated as the lower bound of the transition zone from adsorption to capillarity. Akin and Likos (2017) observed a minimum tensile strength of kaolinite disks around RH = 0.8 and estimated that this unique RH point denotes the transition from adsorption to capillarity. Their RH value is more likely to describe the middle point of the transition zone, where the capillary effective stress increase with water content starts to outcompete the adsorptive effective stress decrease with water content. As such, it is reasonable that the predicted RH value of 0.46 for Georgia kaolinite is lower than their RH = 0.8.

The calculated monolayer coverage RH on the internal surface (RH\textsubscript{m-int}) is different from that on the external surface (RH\textsubscript{m-ext}), shown in Table 2. Both RH\textsubscript{m-ext} and RH\textsubscript{m-int} are directly calculated from Eq. [5] for the external surface and Eq. [6] for the internal surface using the fitted monolayer water contents \(w\textsubscript{m-ext}\) and \(w\textsubscript{m-int}\) shown in Table 2. The calculated RH\textsubscript{m-int} is unfailingly higher than the RH\textsubscript{m-ext} for all soils, suggesting a higher or less negative adsorption free energy on the internal surface. Additionally, the monolayer coverage RH varies significantly with soil type, i.e., for RH\textsubscript{m-ext} from 0.03 to 0.35 and for RH\textsubscript{m-int} from 0.23 to 0.84. Therefore, it can be concluded that monolayer coverage RH varies not only internal or external but also soil type, indicating that the assumption of the existence of a universal monolayer coverage RH made in many previous models for the SSA calculation is incorrect.

The parameter \(c\) (dimensionless) is an increasing function of the adsorption enthalpy (e.g., Pomonis et al., 2004). The predicted \(c\) values on the external surface \((c\textsubscript{ext})\) are invariably higher than those on the internal surface \((c\textsubscript{int})\). This indicates that the adsorption enthalpy on the external surface is generally higher than that on the internal surface, in accordance with the free energy levels discussed above and illustrated in Fig. 2.

The fitted augmented BET equation is illustrated in Fig. 7 with the measured adsorption isotherm data for six representative soils: one kaolinite soil (Georgia kaolinite); two bentonite soils (Wyoming bentonite and Ca-bentonite); one illite soil (Denver claystone); one clayey soil (Wcs Andrews), and one silty soil (Bonny silt). In general, excellent matches were achieved between the measured isotherm data and the augmented BET equation, with a correlation coefficient \(R^2\) of \(\geq 0.95\) for all 25 soils with one exception (see Table 2). In Fig. 7a, water adsorption on Denver claystone is identified by Eq. [7] as completely contributed by the external surface adsorption. The internal surface adsorption noticeably participates in adsorbing water on the Wcs Andrews, Bonny silt, and Georgia kaolinite soils, showing consistency with their low expansibility (i.e., low plasticity index values), as illustrated in Fig. 7b to 7d. Georgia kaolinite is a typical 1:1 mineral, however, and is predicted to exhibit internal surface adsorption. Such internal surface adsorption may be interpreted as the adsorption of water molecules on the contact area between the very fine clay particles. In contrast, water adsorption on the Ca-bentonite and Wyoming bentonite is identified by Eq. [7] as dominated by internal surface adsorption, consistent with their high expansibility.

Fig. 7. Fitted augmented Brunauer–Emmett–Teller (BET) equation for water adsorption isotherms of (a) Denver claystone, (b) Wcs Andrews soil, (c) Bonny silt, (d) Georgia kaolinite, (e) Ca bentonite, and (f) Wyoming bentonite; RH is relative humidity.
Nitrogen Adsorption Isotherm

The N\textsubscript{2} adsorption isotherm was used to verify the augmented BET equation's ability to separate internal and external surface adsorption. The N\textsubscript{2} adsorption isotherm is the relationship between the amount of adsorbed N\textsubscript{2} (volume) and the relative pressure of N\textsubscript{2} (partial pressure divided by the equilibrium pressure). The N\textsubscript{2} molecule is nonpolar and inert to electrical fields generated by cations and particle surfaces. No driving force such as cation hydration is available for N\textsubscript{2} to overcome the interlamellar van der Waals attraction (e.g., Aylmore, 1970; Ravikovitch et al., 2005; Zhang and Lu, 2018b). Therefore, the N\textsubscript{2} molecule is unable to penetrate into the interlamellar space of clay minerals. It is therefore expected that the N\textsubscript{2} adsorption isotherm on soils is fully determined by external surface adsorption (e.g., Heister, 2014). Here, the augmented BET equation was assessed for whether it can predict the external surface dominating feature of N\textsubscript{2} adsorption.

Generally, the augmented BET equation can well represent the N\textsubscript{2} adsorption isotherm data for Georgia kaolinite and Wyoming bentonite, with $R^2 \geq 0.97$, as shown in Fig. 8. The parameters determined via best fits are summarized in Table 2, indicating zero monolayer gas content adsorbed on the internal surface. That is, the augmented BET equation predicts that the N\textsubscript{2} isotherms for both soils are fully dominated by external surface adsorption, showing consistency with the existing experimental and theoretical evidence (e.g., Heister, 2014). Here, the augmented BET equation was assessed for whether it can predict the external surface dominating feature of N\textsubscript{2} adsorption.

Specific Surface Area Estimation

The SSA estimation is one of the main motivations for conducting sorption isotherm measurement. Two independent methods for calculating SSA are used for comparison: the EGME isotherm by the BET equation (Akin and Likos, 2016) and SMC (Khorshidi et al., 2017). As discussed above, the SSA can be estimated from the monolayer water content, and the physical linkage between the SSA and the monolayer water content depends on whether the water is retained in the internal or external surface (e.g., Akin and Likos, 2016; Khorshidi et al., 2017). As demonstrated in Eq. [7], the augmented BET equation can describe monolayer water content on both the external and internal surfaces. Thus, there is no need to presume whether soils are non-swelling or swelling, as required for the existing methods for SSA calculation. Accordingly, the total SSA can be calculated as the sum of the estimated external SSA\textsubscript{ext} and internal SSA\textsubscript{int}:

\[
\text{SSA} = \frac{w_{m\text{-ext}} + 2w_{m\text{-int}}}{M_w} N_A A_m \tag{8}
\]

\[
\text{SSA}_{\text{ext}} = \frac{w_{m\text{-ext}}}{M_w} N_A A_m \tag{9}
\]

\[
\text{SSA}_{\text{int}} = 2 \frac{w_{m\text{-int}}}{M_w} N_A A_m \tag{10}
\]

The SSA values estimated by the augmented BET equation for the 25 selected soils are shown in Fig. 9a. The estimated SSAs of the soils vary from 22 m\textsuperscript{2} g\textsuperscript{-1} for New Orleans soil to 594 m\textsuperscript{2} g\textsuperscript{-1} for Wyoming bentonite, covering a wide range of soils and variability in SSA. The EGME-based SSA values from Akin and Likos (2014) are shown in Fig. 9a. The SSA values estimated by the augmented BET equation generally well match those by the EGME method, with $R^2 = 0.93$. The small discrepancy between the two methods can be attributable to the unequal interfacial properties of water molecules and EGME molecules (e.g., Quirk and Murray, 1999; Akin and Likos, 2014). Because the SSA by the augmented BET equation is obtained from the water adsorption isotherm, it is more appropriate to represent the soil-water related properties.

Recently, Khorshidi et al. (2017) developed a soil moisture capacity (SMC) based method to estimate the SSA from water adsorption isotherms. Figure 9b shows the SSA values estimated by the augmented BET against those by the SMC. The SMC method follows the general trend of the SSA estimated by the augmented BET, with $R^2 = 0.87$, but tends to yield higher SSA values, showing a consistent pattern with the comparisons between SMC and EGME (Khorshidi et al., 2017). Significant discrepancies up to 52% for K bentonite are observed between the SMC and EGME methods.
methods (Khorshidi et al., 2017), whereas the discrepancy between the augmented BET and the EGME method is <40%. In this sense, the estimation by the augmented BET equation is more reliable than that by the SMC.

**Summary and Conclusions**

An augmented BET equation was established to delineate the isotherm of water adsorbed on soils. The rationale underpinning this equation is that water adsorption on soils cannot be well captured by the original BET equation due to the significant spatial heterogeneity of adsorption energy between the external (particle) surface and internal (intra-crystalline) surface. This adsorption energy heterogeneity is recognized as the disparity in free energy levels between the external and internal surface adsorption, physically stemming from the additional van der Waals and electrostatic attraction between lamella involved in the internal surface adsorption. The augmented BET equation can quantitatively describe two independent adsorption processes: the external (particle) surface adsorption and internal (intra-crystalline) surface adsorption. As such, the augmented BET equation overcomes the incapability of the original BET equation in describing the nonlinear behavior exhibited in the soil-water isotherm in the BET plot space. The equation explicitly involves the physical parameters of the external and internal surface monolayer water contents, enabling its ability to predict or quantify the external and internal surface areas.

The augmented BET equation can well represent the measured isotherms of water adsorption on a variety of silty and clayey soils from the literature, validating its applicability and accuracy. Additionally, the non-polar N\textsubscript{2} adsorption isotherms of Georgia kaolinite and Wyoming bentonite can be well fitted by the augmented BET equation, yielding the dominant external surface adsorption and thus further verifying its accuracy. The accuracy of the equation in estimating the SSA has been further verified by comparing with the independent EGME method and the SMC method. The augmented BET equation improves SSA estimation from adsorption isotherms in (i) overcoming the previous subjective presumption of either non-expansive or expansive soils; (ii) avoiding the determination of the monolayer coverage relative humidity that is subject to non-uniqueness; and (iii) providing a universal and objective way to estimate both the external and internal SSA.
A salient feature of the augmented BET equation is its ability to determine both the external and internal surface areas by a soil’s measured water adsorption isotherm data, thus providing a convenient and comprehensive approach to estimate SSA values for soils in routine practice. Because the interplay between the external and internal surface adsorption can be quantitatively separated by the augmented BET equation, it opens new ways to explicitly characterize the microscale soil–water interaction energies within the interlamellar space and to quantify the energy source for intercrystalline swelling and the physical properties of interlamellar adsorption water.

Acknowledgments
This research was sponsored by National Science Foundation grants CMMI-1363515 and CMMI-1561764.

References

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