

Article

An Alternative Approach to the Saturation Behavior of Adsorption Isotherms

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Abstract

Experimentally, adsorption is usually described by adsorption isotherms, which present a saturation effect at high enough concentration or pressure of the adsorbate fluid. This well-known saturation effect was first theoretically discussed by Langmuir, and it is commonly attributed to the finite number of adsorption sites on the substrate surface. Here, we propose an alternative approach to introduce saturation via a repulsive interaction potential, ϕ , among the adsorbate particles, in addition to the attractive potential between the adsorbate particles and the substrate. Using the proposed toy model for a semi-infinite sample, we calculate adsorption isotherms for a typical van der Waals interaction potential. The concentration profile of the adsorbate as a function of the distance from the surface is calculated for several bulk concentrations. The functional dependence of the saturation concentration on the strength of the repulsive inter-particle interaction is extracted by fitting numerical data. Our results are compared to those of the Langmuir model. No assumption of a finite predefined number of adsorption sites is required to obtain saturation.

Keywords: Langmuir isotherm; adsorption saturation; inter-adsorbate interactions; adsorbate-adsorbent interaction; continuous approach

1. Introduction

Adsorption is a fundamental surface phenomenon whereby particles (atoms, ions, molecules) from a fluid phase accumulate on the surface of a solid or liquid substrate, the adsorbent, and form a simple or multilayer film on the surface [1–4]. The relationship between the amount of a substance adsorbed on a surface and its equilibrium concentration or pressure in the bulk, measured at a constant temperature, is called an adsorption isotherm. Adsorption is typically an exothermic process that depends strongly on temperature. Adsorption is a universal surface phenomenon that governs how materials interact with their environment. From thin-film deposition and self-assembly to detergency, sensing, and electrochemistry, adsorption defines the structure, reactivity, and functionality of interfaces. It therefore represents one of the most pervasive and interdisciplinary concepts in modern science and technology. The role of adsorption is central to a variety of natural and industrial processes, including heterogeneous catalysis, gas storage, wastewater treatment, and environmental pollution control [5–12].

Several adsorption isotherm models have been proposed since the beginning of the 20th century. Among the most widely applied are the Langmuir isotherm [13–15], which



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assumes monolayer adsorption on a homogeneous surface with a finite number of identical sites, and the Freundlich isotherm, an empirical model which is not physically founded and that accounts for adsorption on heterogeneous surfaces with a non-uniform energy distribution [16]. Other models, such as the Temkin [17] and BET (Brunauer–Emmett–Teller) isotherms [18], extend these concepts to include adsorption potential dependence on the adsorbate amount and multilayer adsorption phenomena. These models and their generalizations [19–22] provide valuable insights into adsorption mechanisms, surface properties, and the thermodynamic parameters governing the process. A detailed review on adsorption models is given in [23–28].

Considering the atomic structure of a surface, the Langmuir’s model assumes that adsorption occurs on a homogeneous surface with a finite number of identical sites, each capable of holding one particle, and that there is no interaction between adsorbed species. The model further assumes a dynamic equilibrium between adsorption and desorption processes. The rate of adsorption is proportional to both the pressure (or concentration) of the adsorbate and the fraction of vacant sites, while the rate of desorption is proportional to the fraction of occupied sites. At equilibrium, the rates of adsorption and desorption are equal, leading to the classical Langmuir expression:

$$\theta = \frac{KP}{1 + KP} \quad (1)$$

where θ is the fractional surface coverage, P is the gas pressure (or concentration C in solution), and K is the equilibrium constant of adsorption. As $P \rightarrow \infty$, $\theta \rightarrow 1$, indicating that all adsorption sites are occupied, this represents the condition of saturation. Saturation in the Langmuir model reflects the limited number of adsorption sites on the surface. When each site is occupied by one adsorbate molecule, the surface cannot accommodate any additional molecules, and the adsorption rate becomes zero. Any further increase in adsorbate concentration does not increase the number of adsorbed particles, producing the characteristic plateau in Langmuir-type adsorption isotherms.

Discrete-site adsorption models, such as the Langmuir, Fowler–Guggenheim, and Frumkin isotherms, as well as Hill, Ising, and other lattice-based approaches, require prior knowledge of the total number of adsorption sites. However, there exists a broad class of materials for which well-defined adsorption sites cannot be identified. These systems may be described by continuous adsorption models. Such behavior is characteristic of amorphous materials (e.g., glasses), low-surface-energy materials dominated by van der Waals interactions and lacking directional chemical bonding, and liquid and soft interfaces, including polymeric materials. For these systems, the number of adsorption sites cannot be predefined.

In the present paper, we propose an alternative perspective that results in the saturation effect without assuming a limiting number of active sites for adsorption on the adsorbent surface in contact with a fluid reservoir; that is, the proposed toy model functions within the continuous-media approximation for the adsorbent substrate. The mechanism that introduces saturation is the repulsive inter-adsorbate-particle interaction, which, in general, could be of steric nature or arise from a distant-effective interaction between adsorbate particles in the presence of the fluid solvent and the substrate. In Section 2, we recall briefly the state of the art. In Section 3, we present our toy model and the derived results. Finally, Section 4 is devoted to discussion and conclusions.

2. Current Approach (Discrete Case)

The adsorption phenomenon is related to the presence of surface forces responsible for an increase or decrease in the particles’ concentration close to a limiting surface. The

effect is present in all limited systems, and the surface forces could be due to a direct interaction of the particles with the substrate or to the incomplete interaction between the bulk molecules. There are several phenomenological models proposed to describe the adsorption phenomenon of bulk molecules from a surface, as discussed in the introduction. In all models, the concept of the bulk density of adsorbable particles (particles per unit volume), n , is introduced, along with the surface density of adsorbed particles (particles per unit surface), σ , and a kinetic equation for the time variation of the surface density is built in terms of n and σ . Since adsorption is a dynamical phenomenon depending on the adsorption of particles from the bulk and the desorption of particles from the surface, in general, the kinetic equation is of the kind

$$\frac{d\sigma}{dt} = \mathcal{A}(n, \sigma) - \mathcal{D}(n, \sigma), \quad (2)$$

where $\mathcal{A}(n, \sigma)$ and $\mathcal{D}(n, \sigma)$ describe the adsorption and desorption phenomena, and n is the bulk density of adsorbable particles just in front of the adsorbing surface. In the state of equilibrium, $d\sigma/dt = 0$, and the values of equilibrium of n and σ , which we indicate by n_{eq} and σ_{eq} , are such that

$$\mathcal{A}(n_{eq}, \sigma_{eq}) = \mathcal{D}(n_{eq}, \sigma_{eq}). \quad (3)$$

The actual values of n_{eq} and σ_{eq} are determined by taking into account the conservation of particles or the presence of an external reservoir.

In the latter case of the presence of an external reservoir fixing $n_{eq} = n_b$, from (3), it is possible to derive σ_{eq} . In this case, the sample under investigation is not a closed system, since it can exchange particles with the reservoir.

On the contrary, if the system is a closed system, the number of adsorbate particles remains constant. In the simple situation in which the sample is a slab of thickness d limited by two identical adsorbing surfaces, the conservation of the particles is

$$2\sigma_{eq} + n_{eq}d = n_b d, \quad (4)$$

where n_b is the bulk density of particles in the absence of adsorption, and it has been supposed that in the equilibrium state, the bulk density of particles is homogeneous across the sample. This hypothesis is based on the assumption that the surface forces are of short range.

From Equation (3), it follows that for small variations from the equilibrium state, $\delta n = n - n_{eq} \ll n_{eq}$ and $\delta\sigma = \sigma - \sigma_{eq} \ll \sigma_{eq}$, the time variation of σ is given, at the first order in δn and $\delta\sigma$, by

$$\frac{d\delta\sigma}{dt} = K \delta n - H \delta\sigma, \quad (5)$$

where

$$K = \left(\frac{\partial \mathcal{A}}{\partial n} - \frac{\partial \mathcal{D}}{\partial n} \right)_{n_{eq}, \sigma_{eq}}, \quad H = - \left(\frac{\partial \mathcal{A}}{\partial \sigma} + \frac{\partial \mathcal{D}}{\partial \sigma} \right)_{n_{eq}, \sigma_{eq}}. \quad (6)$$

A widely used kinetic equation to describe adsorption phenomenon is the one proposed by Langmuir:

$$\frac{d\sigma}{dt} = k n - \frac{1}{\tau} \sigma, \quad (7)$$

where k , with units of m/s , and τ , with units of s , are phenomenological parameters known as the adsorption coefficient and desorption time. For $\tau \rightarrow \infty$, the surface does not desorb, and σ increases with the time. The adsorption term is proportional to the bulk density of particles just in front of the adsorbing surface n , and the desorption time is proportional to

the surface density of adsorbed particles σ . Equation (7) is similar to (6). Hence, it can be considered as an approximation of a more general adsorption kinetic equation.

In the case in which a reservoir is present, and $n_{\text{eq}} = n_b$, Equation (7) can be rewritten as

$$\frac{d\sigma}{dt} = k n_b - \frac{1}{\tau} \sigma, \quad (8)$$

and the time evolution of $\sigma(t)$ can be easily determined. In this case, $\sigma(t)$ tends to the equilibrium value

$$\sigma_{\text{eq}} = k \tau n_b, \quad (9)$$

with a relaxation time τ . From (9), it follows that for $n_b \rightarrow \infty$, $\sigma_{\text{eq}} \rightarrow \infty$.

By contrast, if the sample is a closed system in the shape of a slab, and assuming the validity of Equation (4) for all t , i.e., $2\sigma(t) + n(t)d = n_b d$, Equation (7) can be rewritten as

$$\frac{d\sigma}{dt} = k n_b - \left(\frac{1}{\tau} + 2 \frac{k}{d} \right) \sigma. \quad (10)$$

From (10), we get that, in the considered approximations, the effective desorption time depends on the thickness of the sample, and it tends to τ for $d \rightarrow \infty$. In the equilibrium state, n_{eq} and σ_{eq} are found to be

$$\sigma_{\text{eq}} = \frac{k\tau}{1 + 2(k\tau/d)} n_b, \quad \text{and} \quad n_{\text{eq}} = \frac{n_b}{1 + 2(k\tau/d)}. \quad (11)$$

From (9) and (11), it follows that $\ell = k\tau$ is a characteristic length related to the adsorption. In the presence of a reservoir, σ_{eq} coincides with the adsorption of particles contained in the surface layer of thickness ℓ . In the case in which the sample is a slab, from (11), it follows that for $\ell \rightarrow \infty$, i.e., $\ell \gg d$, $\sigma_{\text{eq}} \rightarrow n_b d/2$ and $n_{\text{eq}} \rightarrow 0$; i.e., all the adsorbable particles are adsorbed by the limiting surfaces. The expression for σ_{eq} in Equation (11) indicates that, for fixed k and τ , $\sigma_{\text{eq}} \propto n_b$. However, since the adsorbed particles are not point-like, σ_{eq} given by (9) or (11) cannot increase without limit. The considered model is then valid in the limit of small n_b , i.e., for diluted solutions.

In the case of large n_b , it is necessary to modify (7) in such a manner that σ_{eq} tends to a limiting value for $n_b \rightarrow \infty$. The simplest generalization of (7) to describe saturation effects is [29]

$$\frac{d\sigma}{dt} = k \left(1 - \frac{\sigma}{\sigma_0} \right) n - \frac{1}{\tau} \sigma, \quad (12)$$

where σ_0 is the maximum surface density of adsorbed particles, related to the adsorption mechanism. It could be called the surface density of adsorbing sites. The phenomenological expression (12) in the limit of $\sigma \rightarrow \infty$ gives (7).

In the presence of a reservoir, since $n_{\text{eq}} = n_b$, from (12), the equilibrium value of the surface density of adsorbed particles is

$$\sigma_{\text{eq}} = \frac{k \tau n_b}{1 + k \tau n_b / \sigma_0}, \quad (13)$$

which, for $\sigma_0 \rightarrow \infty$, reduces to (9).

In the case where the sample is a slab, taking into account condition (4) on the conservation of particles, in the equilibrium state from (12), we get for σ_{eq}

$$\frac{\sigma_{\text{eq}}}{\sigma_0} = \frac{1 + u(1+r)}{2u} \sqrt{\left(\frac{1 + u(1+r)}{2u} \right)^2 - r}, \quad (14)$$

where $u = 2k\tau/d$, $r = \sigma_M/\sigma_0$, and $\sigma_M = n_b d/2$ is the maximum value of the adsorbed particles for the given solution and sample. The influence of the saturation effects described by the kinetic equation (12) on the time evolution toward the equilibrium state has been discussed in [30]. Of course, Equation (14) is one possible generalization of Equation (7) derived by

$$\frac{d\sigma}{dt} = k \left\{ 1 - \left(\frac{\sigma}{\sigma_0} \right)^p \right\} n - \frac{1}{\tau} \sigma, \quad (15)$$

with $p \geq 1$ [30]. Of some interest is the case with $p = 2$, which could be related to the case in which the adsorbate particles are electrically charged.

The generalizations of (7) along the line described above are completely phenomenological. It is based on the obvious idea that the surface density of adsorbed particles in concentrated solutions has to tend to a saturation value σ_0 . Consequently, the effective adsorption coefficient has to change sign for $\sigma > \sigma_0$. Instead, to attribute the origin of σ_0 to the finite number of adsorbing sites on the surface, the origin of σ_0 could be attributed to the repulsive forces between the adsorbed particles. The goal of our investigation is to relate σ_0 to this repulsive part of the interaction.

3. An Alternative Approach (Continuous System)

As stressed above, the Langmuir Equation (7) and its generalization (15) are phenomenological and based on plausible arguments, without considering the forces responsible for the adsorption. In the absence of adsorption, the bulk density of adsorbate is homogeneous. The presence of an adsorbing substrate introduces a surface field, localized close to the substrate and vanishing in the bulk, which is responsible for a position dependence of the adsorbate density that approaches its equilibrium value far enough from the surface. In the steady state, the drift current of particles balances the diffusion current, and the bulk density profile is given by the Boltzmann distribution. A description of the adsorption phenomenon based on the concept of adsorption energy can therefore be formulated within the framework of statistical mechanics [31–34]. The aim of the present section is to analyze the adsorption phenomenon using Boltzmann statistics, introducing an adsorption energy that contains both attractive and repulsive contributions, and relaxing the condition of a predefined number of adsorptions sites. The attractive term accounts for the interaction between the adsorbate particles and the adsorbent substrate, while the repulsive term represents the inter-particle interactions.

In this context, let us consider the half-space approximation, with the z -axis originating at the adsorbing surface. The adsorption phenomenon is related to a potential energy, indicating that for the particles, it is energetically more favorable to remain near the surface than in the bulk. If $V = V(z)$ is the potential energy, arising, for instance, from van der Waals interactions, the steady-state distribution of particles is given, according to Boltzmann statistics, by

$$n(z) = n_b e^{-\beta V(z)}. \quad (16)$$

where n_b is the bulk density in the absence of adsorption, and $\beta = 1/k_B T$ is the inverse thermal energy. When $V(z)$ does not depend on the adsorbed particles, $n(z)$ is the solution of the problem. If $V(z)$ is strongly peaked near the surface, like a kind of Dirac-like function, $n(z)$ becomes very large close to $z = 0$ and rapidly approaches n_b as z increases. We denote by λ the range of $V(z)$, defined by $V(z) \neq 0$ for $0 \leq z \leq \lambda$, and $V(z) = 0$ for $z > \lambda$. The rapid decay of $n(z)$ allows us to define a surface density of particles, due to the adsorption via the relation

$$\sigma = \int_0^\lambda [n(z) - n_b] dz. \quad (17)$$

In this way, it is possible to relate the adsorption coefficient k entering in (7) with the adsorption energy [35].

All these considerations are straightforward and well known, and so far we have not introduced the concept of available adsorption sites. To proceed further, we can assume that the adsorption energy depends on $n(z)$. In the simple case of electro-adsorption [29], the effective surface field is $E_0 - q\sigma/\varepsilon$, where E_0 is the external electric field and $q\sigma/\varepsilon$ is the reaction field. In the case of pure adsorption, that is, in the absence of an external field, the potential energy per particle, $V_0(z)$, describing the adsorption, can be well approximated by

$$V_0(z) = -\frac{A}{(1 + z/\xi)^3}, \quad (18)$$

where A is related to the Hamaker constant, and ξ is the characteristic length of the interaction between the adsorbate particles in the bulk and the substrate. If the effective adsorption energy depends on $n(z)$, through a repulsive inter-particle interaction $\phi[n(z)]$ (such as electrostatic or hard-sphere interactions), the mean field acting on the particle is then given by

$$V(z) = V_0(z) + \phi[n(z)]. \quad (19)$$

In this framework, Equation (16) has to be rewritten as

$$n(z) = n_b e^{-\beta[V_0(z) + \phi[n(z)]]}, \quad (20)$$

from which it follows that the equilibrium distribution of particles is

$$n(z) e^{\beta\phi[n(z)]} = n_b e^{-\beta V_0(z)}. \quad (21)$$

Equation (21) allows us to define a new σ , and consequently a new adsorption coefficient, without introducing the concept of discrete adsorption sites, which is inconsistent with a continuum description. The task now is to express the potential ϕ as a function of $n(z)$. For electrostatic interactions, the analysis is simple because the electric field is determined by the charge density through the Poisson equation, whereas for neutral particles, an explicit form of $\phi[n(z)]$ must be found. Deep in the bulk, where $V_0(z) = 0$, the equilibrium density of particles is n_b . This implies that $\phi(n_b) = 0$. Consequently, we can write $\phi(n) = \phi(n - n_b)$; i.e., ϕ depends on the deviation of the particle density from its equilibrium value in the bulk and therefore its dependence on z is indirect via $n(z)$. In a first-order expansion around the bulk density, $\phi(n - n_b)$ can be written as

$$\phi(n - n_b) = \alpha[n(z) - n_b], \quad (22)$$

where α depends on the inter-particle interaction which, hereafter, is assumed to be repulsive ($\alpha > 0$) to exclude aggregation effects. At this point, we note that the linear approximation adopted for $\phi(n - n_b)$ does not imply a simple linear spatial interaction among adsorbate particles. In this framework, the bulk density of particles is given by

$$n(z) = n_b e^{-\beta\{V_0(z) + \alpha[n(z) - n_b]\}}. \quad (23)$$

Equation (23) is a nonlinear implicit algebraic equation for $n(z)$ and it was solved numerically on a discrete grid using the secant method (Python/SciPy), with cross-checks using secant and Newton methods in Mathematica and working precision between 20 and 50 digits. Convergence required: (i) $n(z) > 0$, (ii) number of iteration less than 80, (iii) solver reported convergence, (iv) absolute and relative tolerances of 10^{-8} . For the numerical calculations presented below, we chose for the potential $V_0(z)$ the van der Waals expression given by Equation (18). Energy is measured in units of $k_B T$, and lengths in

units of ζ , so that $z/\zeta = \zeta$. For the numerical calculations, the values $A = 2k_B T$ and $\alpha = 1k_B T m^3$ were used. Figure 1 shows the reduced density profile $u(\zeta) = n(\zeta)/n_b$ for different values of the bulk adsorbate density n_b . The particle density presents an abrupt variation near the limiting surface, and its profile decreases with the distance from the substrate. As n_b increases, the relative variation of $n(0)/n(\infty)$ decreases monotonically.

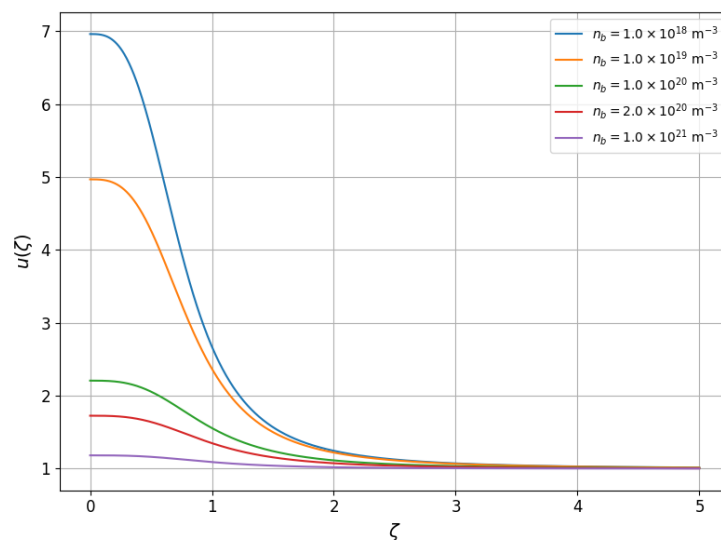


Figure 1. Iso- n_b curves of the spatial profile for the reduced adsorbate concentration $u(\zeta) = n(\zeta)/n_b$ vs. $\zeta = z/\zeta$. The relative surface excess, $u(0)$, of n in respect to the bulk density n_b reduces with increasing n_b .

Now, if we define the surface density of particles by means of Equation (17), it becomes possible to investigate the dependence of σ on n_b . Figure 2 shows σ as a function of n_b , assuming for A , α , and ζ the same values used to draw Figure 1.

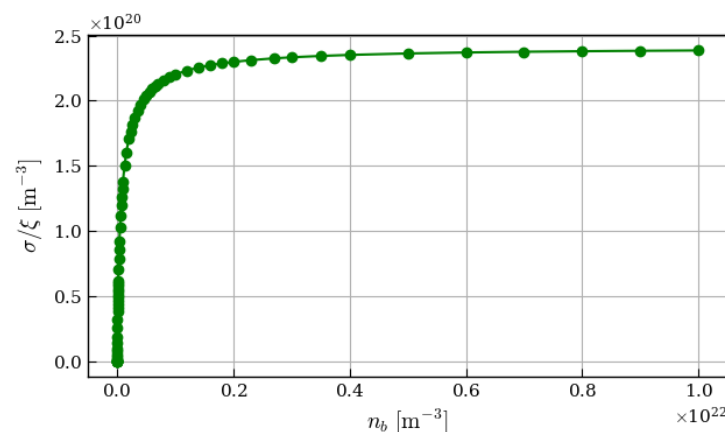


Figure 2. Surface concentration σ over the characteristic length ζ of the attractive potential vs. the bulk density n_b of the adsorbate. For low bulk concentrations, σ goes linearly with n_b , while for large bulk concentrations, saturation appears.

From this figure, it follows that σ is proportional to n_b for low values of n_b , while for large enough n_b , it approaches a limiting value σ_{sat} . This saturation effect is related to the reaction field $\phi(n - n_b)$. Note that no assumption of a limited number of adsorption sites on the substrate has been introduced. A 3D representation of the surface $u(\zeta, n_b)$ is given in Figure 3.

The impact of the reaction potential strength α on saturation is shown in Figure 4, where σ/ζ is plotted against n_b for several representative values of α , measured in $k_B T m^3$

units. When $\alpha = 0$ (dashed line), σ increases linearly with n_b without bound (case of non-interacting point-like particles). When $\alpha > 0$, saturation always appears, and its value σ_{sat} decreases as the strength of the inter-particle potential increases.

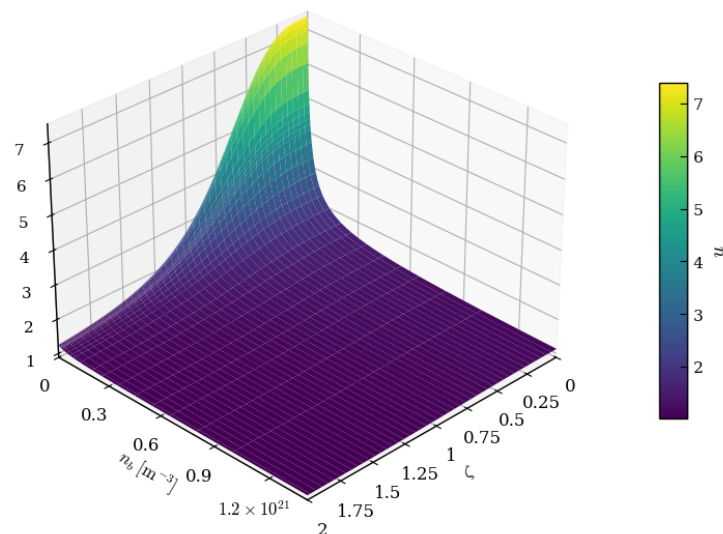


Figure 3. The reduced variation of the adsorbate concentration u vs. the reduced distance ζ from the adsorbent surface and the bulk concentration of the adsorbate n_b .

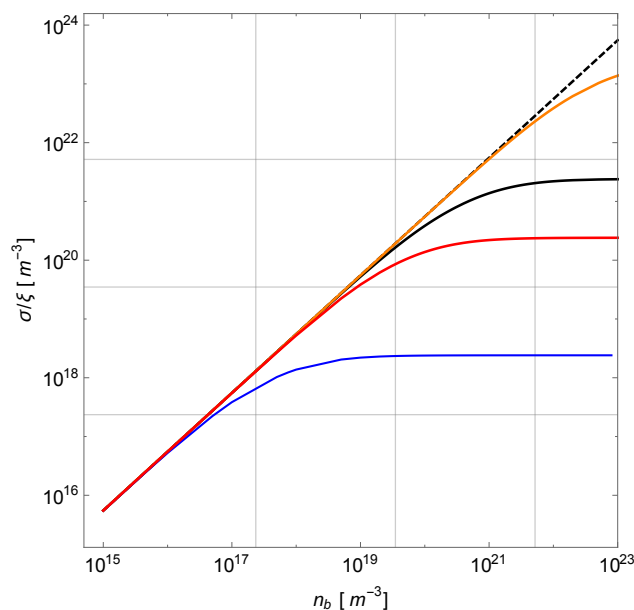


Figure 4. Surface density of adsorbed particles σ versus the bulk density of particles n_b . For diluted solutions (small n_b), $\sigma \propto n_b$, as predicted by Langmuir's isotherm (9). On the contrary, for large n_b values, $\sigma \rightarrow \sigma_{\text{sat}}$. σ_{sat} decreases with increasing strength of the inter-particle potential α . Dashed line for $\alpha = 0$, orange curve for $\alpha = 0.001$, black curve for $\alpha = 0.1$, red curve for $\alpha = 1$, and blue curve for $\alpha = 100$. α is measured in $k_B T m^3$ units.

In the following, we use the numerical data to determine the dependence of σ_{sat} on α . Figure 5 shows the logarithm of σ_{sat} as a function of the logarithm of the reaction field strength α in Equation (22) over a range of eight decades. Solid points are numerically calculated, while the continuous line is a fitting performed by using the expression

$$\sigma_{\text{sat}}/\xi = \frac{p}{(q + \alpha)^w}. \quad (24)$$

The fit gives $p = 10^{20.3809 \pm 0.0004} k_B T$, $w = 0.9998 \pm 0.0002$ and $q \rightarrow 0$. Hence, we conclude that $\sigma_{\text{sat}} \propto 1/\alpha$, as expected, since for $\alpha \rightarrow 0$, $\sigma_{\text{sat}} \rightarrow \infty$, recovering the ideal gas limit. The fit residuals are given in Figure 6.

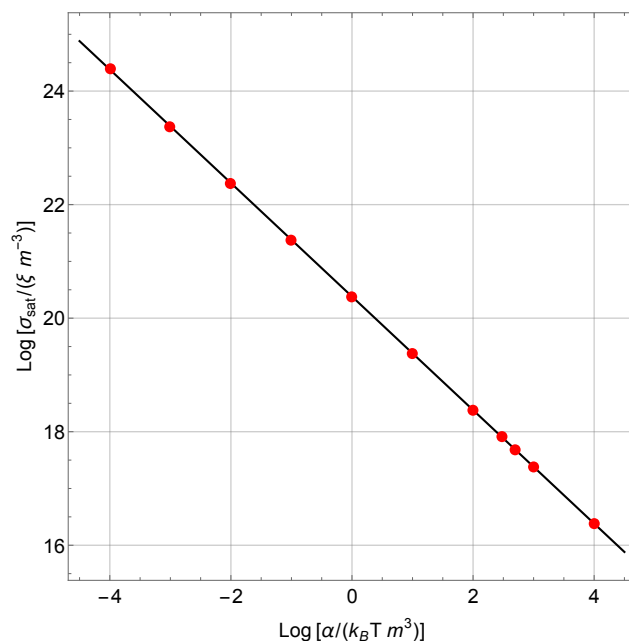


Figure 5. log-log representation of σ_{sat} vs. α . Points: numerical determination of σ_{sat} ; continuous curve: fitting function given by Equation (24). σ_{sat} is proportional to $1/\alpha$, indicating that the reaction field is responsible for the saturation of σ .

A word of caution is necessary here. The above scaling law, $\sigma_{\text{sat}} \propto \alpha^{-1}$, is valid in the linear approximation of the potential ϕ in powers of $[n(z) - n_b]$. This scaling law is not expected to be valid if a quadratic term in the expansion is kept, for this second-order term cannot be treated as a perturbation. As shown in Figure 7, when the second-order term is kept, that is

$$\phi(n - n_b) = \alpha[n(z) - n_b] + \frac{1}{2}\alpha_2[n(z) - n_b]^2 \quad (25)$$

then for $\alpha_2 \neq 0$ the saturation level changes. That is, the saturation effect is always present but the above scaling law is modified in the presence of the quadratic term.

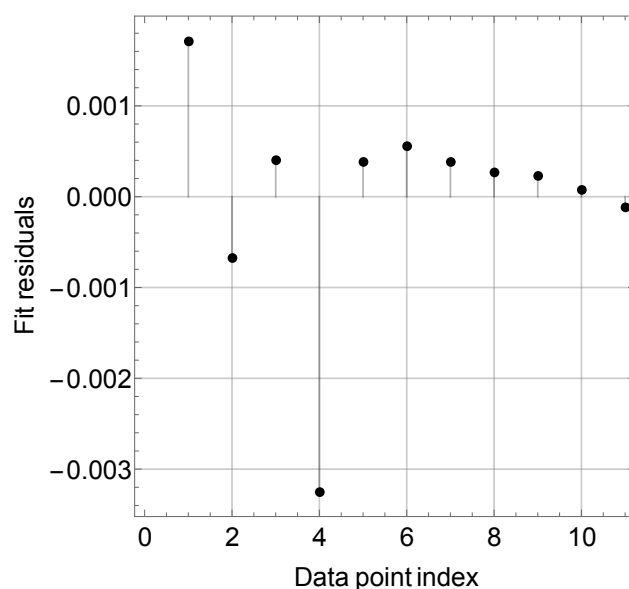


Figure 6. Fit residuals vs. the data point index, for the fit shown in Figure 5.

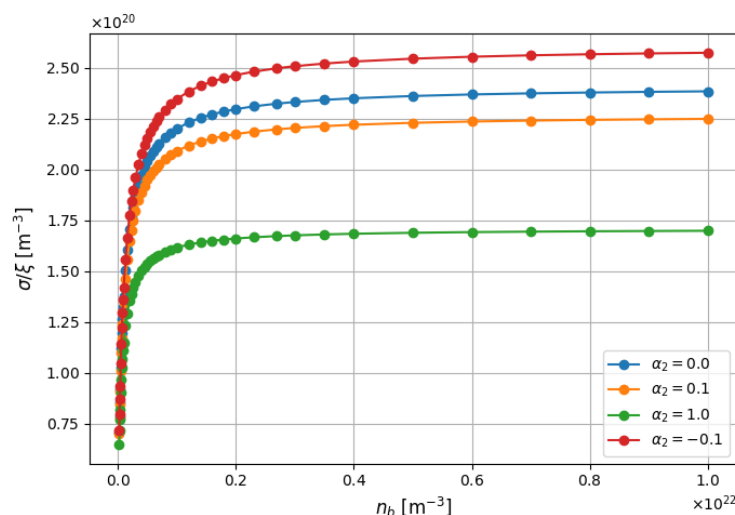


Figure 7. Surface concentration of the adsorbate σ over the characteristic length ξ vs. the bulk density n_b for the quadratic approximation of the inter-particle interaction potential ϕ . At low n_b , σ still increases linearly with n_b , while for large n_b , it approaches saturation. The level of saturation depends on α_2 . The remaining parameter values are the same as in Figure 2. α_2 is measured in $k_B T \text{ m}^6$ units.

4. Conclusions

The adsorption of neutral particles onto a surface from a solution has been reconsidered within a continuum description of the substrate. In the analysis presented above, we considered a short-range particle–substrate interaction of the van der Waals type, with an interaction range of ξ . In this case, the deviation of the adsorbable particle density $n(z)$ from its bulk density n_b , caused by the presence of the surface, is confined to a region close to the adsorbing substrate, within a surface layer whose thickness is on the order of a few ξ . Therefore, the adsorption phenomenon can be described by a surface density of particles, σ , defined as the integral of $n(z) - n_b$ along the surface layer thickness. If only the attractive part of the particle–surface interaction is present, the surface density of adsorbed particles is found to be proportional to the bulk density of adsorbable particles in thermodynamical equilibrium. To avoid this non-physical result, we introduced a repulsive interaction between the adsorbable particles, ϕ , proportional to the density deviation from its equilibrium density in the bulk, $\phi = \alpha(n - n_0)$. Within this framework, the surface density of adsorbed particles is proportional to the bulk density of adsorbable particles only in the case of dilute solutions, whereas it approaches a saturation value, σ_{sat} , for concentrated solutions. Within this simple model, it follows that $\sigma_{\text{sat}} \propto 1/\alpha$. The results obtained show that this present approach reproduces the trend of the phenomenological Langmuir isotherm without its limitation for a finite number of discrete adsorbing positions on the adsorbent. Of course, the substrate–adsorbate interaction potential used in the present analysis can be replaced by another attractive potential, for instance, an exponential one.

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