

Theory of localized adsorption on surfaces undergoing reversible reconstruction

G. F. Cerofolini*

STMicroelectronics, Stradale Primosole 50, 95121 Catania, Italy

(Received 25 September 2002; revised manuscript received 13 January 2003; published 21 April 2003)

A rate equation, which takes explicitly into account the surface reconstruction phenomena occurring (reversibly or irreversibly) while adsorption or desorption proceeds, is proposed. The equation contains a few free parameters which specify the adsorption and desorption rate constants, and the reconstruction and irreversibility degrees of the process. A complete qualitative study of the solutions of the rate equation for a case of reversible and self-similar reconstruction is given.

DOI: 10.1103/PhysRevE.67.041603

PACS number(s): 82.65.+r, 68.43.Mn

I. THE LANGMUIR THEORY

Formulated in 1916, the Langmuir theory of adsorption equilibrium and kinetics has remained unrivaled during the 20th century for its simplicity, elegance, and flexibility [1].

A. The assumptions of Langmuir's theory

Langmuir's theory applies to a submonolayer localized adsorption without lateral interactions and is based on the following assumptions: (L1), one molecule per adsorption site; (L2), absence of intermolecular interactions; (L3), surface homogeneity; (L4), adsorption rate proportional to the amount of empty sites; (L5), desorption rate proportional to the amount of full sites; (L6), gas ideality; (L7), no internal structure of the adsorbed molecules; and (L8), absence of surface reconstruction. Needless to say, if one is interested in equilibrium properties only, the Langmuir isotherm can be derived using a by far less restrictive set of assumptions [2].

In a pictorial view, the Langmuir theory can be summarized by reactions (I_+) and (I_-) sketched in Fig. 1. The rate equations can be deduced from the scheme of Fig. 1 by a direct application of the mass-action law:

$$dN_{\bullet}/dt = AN_{\circ} - BN_{\bullet}, \quad (1)$$

$$dN_{\circ}/dt = -AN_{\circ} + BN_{\bullet}, \quad (2)$$

where N_{\circ} and N_{\bullet} are the amounts per unit area of empty and full sites, respectively, while A and B are the rate constants for adsorption and desorption;

$$A = \sigma_+ \Phi \quad (3)$$

$$= \sigma_+ p / \sqrt{2\pi m k_B T}, \quad (4)$$

$$B = \tau_-^{-1}, \quad (5)$$

with σ_+ the cross section of the adsorption process, Φ the gas-phase flux impinging onto the surface at pressure p and temperature T , k_B the Boltzmann constant, m the molecular mass, and τ_- the lifetime of the desorption process.

Summing member-to-member equations (1) and (2) one gets that the total amount of sites N_s remains unchanged during adsorption, that is,

$$N_s := N_{\circ} + N_{\bullet} = \text{const}; \quad (6)$$

what may change is only their relative occupation. Defining the surface coverage Θ , $\Theta := N_{\bullet}/N_s$, one gets

$$d\Theta/dt = A(1 - \Theta) - B\Theta. \quad (7)$$

Equation (7) can be solved for Θ giving

$$\Theta(t) = \bar{\Theta} + (\Theta_0 - \bar{\Theta}) \exp(-t/\tau_L), \quad (8)$$

where τ_L is the harmonic sum of A and B ,

$$\tau_L^{-1} := A^{-1} + B^{-1};$$

Θ_0 is the initial coverage, $\Theta_0 = \Theta(0)$; and $\bar{\Theta}$ is the equilibrium coverage,

$$\bar{\Theta} = (1 + B/A)^{-1}. \quad (9)$$

Therefore, the Langmuir theory gives explicitly, through Eqs. (8) and (9), the amount N of adsorbed molecules [$N = N_{\bullet}$ because of (L1)] vs time as well as vs the environmental quantities (such as pressure p and temperature T) which control A and B .

Although simple and elegant, the Langmuir theory does however suffer from the most serious difficulty: the kinetics and equilibria of really few systems can be described by Eqs. (8) and (9), respectively. This difficulty would be ruinous were it not for the fact that it is possible to account for most of the experimental behaviors simply relaxing one or the other of the hypotheses (L1)–(L8).



FIG. 1. The reactions at the basis of the Langmuir theory: adsorption is seen as the formation of filled surface sites (denoted with \bullet) by the reaction of empty surface sites (denoted with \circ) with gas-phase molecules M , while desorption is regarded as the reverse process.

*Also at STMicroelectronics, 20041 Agrate MI, Italy. Electronic address: gianfranco.cerofolini@st.com

B. Relaxing the assumptions of the Langmuir theory

The set of assumptions $\{(L1), \dots, (L8)\}$ forms thus a kind of basic kit for the description of adsorption-desorption phenomena; with the substitution of one or more axioms for (L1)–(L8), one can create another scheme able to account for other phenomena: Langmuir himself was aware of this possibility and in the founding paper he considered also the cases of sites which can host more than one adsorbed molecule, adsorbed films more than one molecule in thickness, and heterogenous surfaces [1]. The several descriptions generated while continuing this game cover almost all the observed phenomena. Among them, the following ones may be mentioned: multisite occupation, lateral interactions, surface heterogeneity, and multilayer coverage [3].

Much more difficult to account, in the spirit of Langmuir's isotherm, has been surface reconstruction. This state of affairs is quite disappointing because in many instances, chemisorption results in adsorbate-induced reconstruction [4]. This is especially true for biological systems which are often characterized by an energy landscape with many nearly equivalent minima (associated with different configurations) separated by hills of low activation energies; this situation allows them to undergo reconstruction even after the adsorption of weakly bound species such as water adsorbed via hydrogen bonding or O_2 coordinated to a transition-metal cation. The importance of reconstructing adsorbents is well known in biochemistry, where this phenomenon has occasionally been considered with specific models [5–8]. Very few *general* theoretical approaches have however been proposed to account for surfaces which undergo reconstruction while adsorption proceeds. Two major theoretical schemes have been proposed: the first method was developed (mainly by Landsberg) to account for kinetics [9], while the other method was developed by Cerofolini transporting to equilibrium the Landsberg model. The kinetic approach was mainly developed to explain the Elovich equation (see later); the equilibrium approach was applied to describe adsorption-induced surface reconstruction [10], protein folding-unfolding [11], and clustering and melting in multilayer adsorption [12,13].

II. THE LANDSBERG MODEL FOR ADSORPTION KINETICS ON RECONSTRUCTING SURFACES

The Elovich equation [14] describes a time-logarithmic behavior which is often found to describe adsorption or, though less frequently, desorption phenomena. The Elovich equation applies to so many situations (adsorption or desorption kinetics on solid adsorbents, oxidation of metals, etc.) and systems as to have attracted numerous investigations. The time-logarithm law is usually explained in terms of activation energy increasing linearly with surface coverage because of lateral interactions [15] as well as of fixed energy heterogeneity characterized by a uniform energy distribution [16–19].

In an intriguing paper [9], however, Landsberg formulated an alternative model for the Elovich equation in adsorption, based on the hypotheses that (R1), desorption is negligible; (R2), adsorption occurs via the collision of impinging gas-

phase molecules on empty surface sites; (R3), adsorption is responsible for surface reconstruction via generation of new sites at a rate proportional to the chemisorption rate; (R4), each newly exposed zone has the same topography as the surface from which it was generated; and (R5), the process proceeds with a progressive reduction of the empty sites.

Using the symbols of this work, (R1), (R2), (R3), (R4), and (R5) can be formulated as follows:

$$B=0, \quad (10)$$

$$dN_{\bullet}/dt=AN_{\circ}, \quad (11)$$

$$dN_{\circ}/dt=\beta dN_{\bullet}/dt, \quad (12)$$

$$\beta=bN_{\circ}, \quad (13)$$

$$b<0, \quad (14)$$

where β represents the net empty sites lost per adsorbed molecule (resulting from the difference between the sites filled after adsorption and the ones correspondingly generated), while b is the net area generated after the adsorption of one molecule. This area results from the algebraic sum of the newly generated area (with positive sign) and the filled area (with negative sign).

Combining Eqs. (10)–(13) one gets a differential equation whose solution is

$$N_{\bullet}(t)=-\frac{1}{b}\ln[1-bAN_{\circ}(0)t]. \quad (15)$$

Taking explicitly into account condition (14) [i.e., substituting $-|b|$ for b in Eq. (15)] one eventually gets

$$N_{\bullet}(t)=\frac{1}{|b|}\ln[1+|b|AN_{\circ}(0)t]. \quad (16)$$

Equation (16) has just the logarithmic behavior of the Elovich equation.

The observation that condition (14) is never used in the derivation of Eq. (15) led, however, Cerofolini to consider the hypothesis that this equation holds true for $b>0$ too. This case is qualitatively different from that considered by Landsberg; in fact, while Eq. (16) diverges smoothly (with downward concavity) only for $t\rightarrow+\infty$, Eq. (15) with positive b diverges for $t\rightarrow[1/bAN_{\circ}(0)]_-$, thus providing an example of explosive dynamic system.

In spite of these interesting features (and of the fact that minor changes in Eq. (11) are sufficient to account for another kinetics frequently observed—the time power law [20–22]), the Landsberg model has often been regarded suspiciously because of its following disturbing features.

(i) For no value of its free parameter b , the Landsberg model is reduced to Langmuir theory.

(ii) Kinetic equation (12) links rate to rate rather than rate to concentration, as would be expected from an application of the mass-action law.

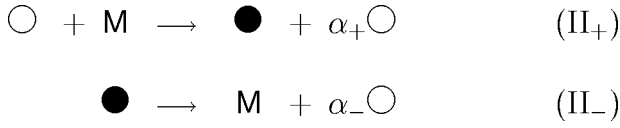


FIG. 2. The reactions at the basis of adsorption models with self-reconstruction. Symbols have the same meaning as in Fig. 1.

(iii) Assumption (R4), specified quantitatively by Eq. (13), appeared (when formulated, in 1952) an *ad hoc* hypothesis difficult to sustain on physical bases.

Even though the appearance of the theory of fractals has made up for the last difficulty (the fact that, while adsorption proceeds, the surface undergoes a reconstruction depending on the preexisting density of sites may be interpreted in terms of a kind of self-similar growth), the above difficulties justify that even accurate reviews of the Elovich equation do not mention the Landsberg model as a possible explanation of the time-logarithm behavior [17].

III. A THEORY FOR ADSORPTION AND DESORPTION ON SURFACES UNDERGOING SELF-SIMILAR RECONSTRUCTION

In view of the ability of the Landsberg model to account for the Elovich equation and its generalization in terms of self-similar growth, it would be interesting to incorporate the Landsberg model in a theory \mathcal{T} such that (i) \mathcal{T} is constructed on the mass-action law; (ii) \mathcal{T} reduces to the Langmuir theory in the absence of reconstruction; and (iii) \mathcal{T} reproduces the Landsberg model in the absence of desorption and for opportune reconstruction.

This incorporation would produce a genuine equilibrium and kinetic theory of *adsorption and desorption on surfaces undergoing self-similar reconstruction*.

A. The dynamic description of surfaces undergoing adsorption-induced reconstruction

Before trying to formulate the theory, we observe that the constancy of the total number of sites $N_{\bigcirc} + N_{\bullet}$ in the Langmuir theory arises from the fact that the total number of sites on the left-hand side (lhs) of the complexive reaction in Fig. 1 coincides with that on the right-hand side (rhs) dynamic systems with surface reconstruction, once sketched with reactions involving empty and filled sites, in general, do not satisfy the above condition.

The dynamic system adopted in this work for describing adsorption and desorption on reconstructing surfaces is sketched in Fig. 2.

For dynamic system $\{(\text{II}_+), (\text{II}_-)\}$, the rate equations are

$$dN_{\bullet}/dt = AN_{\bigcirc} - BN_{\bullet}, \quad (17)$$

$$dN_{\bigcirc}/dt = (\alpha_+ - 1)AN_{\bigcirc} + \alpha_- BN_{\bullet}, \quad (18)$$

where α_+ and α_- are free parameters of the theory.

With *free parameter of a theory* we denote any symbol able to assume any value in a given domain specified by the theory. In particular, any theory of adsorption on reconstruct-

ing surfaces is expected to satisfy the physical condition that the domain of α_+ and α_- is limited from being functions of the state of the surface alone. This condition can be formalized stating that α_+ and α_- (which in general depend on T) once written as functions of N_{\bigcirc} or N_{\bullet} cannot depend on p . For isothermal processes, this condition reads $\partial\alpha_{\pm}/\partial A = 0$ because of Eq. (4).

B. When the parameters allow equilibrium

For any dynamic system, the equilibrium states play a special role. At equilibrium $dN_{\bullet}/dt = 0$ and $dN_{\bigcirc}/dt = 0$ so that an equilibrium state exists if the parameters A , B , α_+ , and α_- are such that the system

$$0 = AN_{\bigcirc} - BN_{\bullet},$$

$$0 = (\alpha_+ - 1)AN_{\bigcirc} + \alpha_- BN_{\bullet} \quad (19)$$

admits a nontrivial solution $(\overline{N_{\bigcirc}}, \overline{N_{\bullet}})$ at least, in addition to the trivial solution $(0, 0)$ which satisfies conditions (19) for all values of the parameters.

Observe now that the total number of sites in an adsorption-desorption cycle $(\text{II}_+) + (\text{II}_-)$ varies by an amount $\alpha_+ + \alpha_- - 1$, so that the surface undergoes a reversible reconstruction when

$$\alpha_+ + \alpha_- = 1, \quad (20)$$

while the reconstruction is irreversible when $\alpha_+ + \alpha_- \neq 1$.

For the search of the equilibrium states, it is convenient to distinguish the *singular case*, in which $\alpha_+ - 1$ is identically null (at least in a nonmeager compact set of the $\{N_{\bigcirc}, N_{\bullet}\}$ plane), from the *general case*, in which $\alpha_+ - 1 \neq 0$.

1. Equilibrium in the singular case

In the singular-case, system (19) is reduced to

$$0 = AN_{\bigcirc} - BN_{\bullet},$$

$$0 = \alpha_- BN_{\bullet}.$$

Excepting the trivial solution, the above equations are mutually compatible only for $\alpha_- = 0$ or for α_- any function $\alpha_-(N_{\bigcirc}, N_{\bullet})$ such that $\alpha_-(N_{\bigcirc}, (A/B)N_{\bigcirc}) = 0$.

2. Equilibrium in the general case

Consider now the general case, with $\alpha_+ - 1 \neq 0$. Let ϵ be the net number of available sites generated per adsorption event,

$$\epsilon = \alpha_+ - 1$$

(ϵ is a kind of *reconstruction degree* of the surface), and δ be the net number of available sites produced in an adsorption-desorption cycle per newly formed site,

$$\delta = \frac{\alpha_+ + \alpha_- - 1}{\alpha_+ - 1} = 1 + \frac{\alpha_-}{\alpha_+ - 1}$$

(δ is a kind of *irreversibility degree* of the process). Taking ϵ and δ as independent variables, Eqs. (17) and (18) become

$$dN_{\bullet}/dt = AN_{\circ} - BN_{\bullet}, \quad (21)$$

$$dN_{\circ}/dt = \epsilon(AN_{\circ} - (1 - \delta)BN_{\bullet}), \quad (22)$$

which reduce to Eqs. (1) and (2), respectively, for $\epsilon = -1$ and $\delta = 0$.

For the dynamic system {(21) and (22)}, the equilibrium conditions (19) read

$$\begin{aligned} 0 &= AN_{\circ} - BN_{\bullet}, \\ 0 &= \epsilon(AN_{\circ} - (1 - \delta)BN_{\bullet}), \end{aligned} \quad (23)$$

with $\epsilon = \epsilon(N_{\circ}, N_{\bullet})$ and $\delta = \delta(N_{\circ}, N_{\bullet})$. Conditions (23) are manifestly compatible when $\delta(N_{\circ}, N_{\bullet})$ is identically null,

$$(\delta(N_{\circ}, N_{\bullet}) = 0) \quad \forall N_{\circ}, N_{\bullet}. \quad (24)$$

Equilibrium is however allowed even when condition (24) is violated, provided (i) irrespective of $\epsilon(N_{\circ}, N_{\bullet})$, the roots of $\delta(N_{\circ}, N_{\bullet}) = 0$ satisfy also the condition $AN_{\circ} = BN_{\bullet}$, in which case the equilibrium state is obtained solving the equation $\delta(N_{\circ}, (A/B)N_{\circ}) = 0$, or (ii) irrespective of $\delta(N_{\circ}, N_{\bullet})$, the roots of $\epsilon(N_{\circ}, N_{\bullet}) = 0$ satisfy also the condition $AN_{\circ} = BN_{\bullet}$, in which case the equilibrium state is obtained solving the equation $\epsilon(N_{\circ}, (A/B)N_{\circ}) = 0$.

Unless the functions $\epsilon(N_{\circ}, N_{\bullet})$ and $\delta(N_{\circ}, N_{\bullet})$ are specified, it is impossible to state anything about their zeros.

For a large class of functions $\epsilon(N_{\circ}, N_{\bullet})$ of physical interest, the roots of the equation $\epsilon(N_{\circ}, N_{\bullet}) = 0$ are either trivial [e.g., $\epsilon(N_{\circ}, N_{\bullet}) = \gamma^2 N_{\circ} + \gamma'^2 N_{\bullet}$, with γ and γ' arbitrary constants] or even unphysical [e.g., $\epsilon(N_{\circ}, N_{\bullet}) = \gamma^2$]. For these functions, equilibrium is possible either for $\delta(N_{\circ}, N_{\bullet})$ identically null (that implies reversible reconstruction) or for states along which the system undergoes reversible reconstruction.

C. Specializing the description to surfaces undergoing reversible reconstruction

Let \mathcal{R} denote the theory described by Eqs. (17) and (18) with α_+ and α_- given functions of N_{\circ} and N_{\bullet} . Since theories with no equilibrium states are of scarce interest, an analysis for the case of reversible reconstruction shall be developed.

Even the dynamics of surfaces undergoing adsorption-induced reconstruction is better considered analyzing the singular case separately from the general case.

1. Dynamics in the singular case

In the singular case, the dynamics of adsorption on surfaces undergoing reversible reconstruction is described by putting $\alpha_+ - 1 = 0$ and $\alpha_- = 0$ in Eqs. (17) and (18):

$$dN_{\bullet}/dt = AN_{\circ} - BN_{\bullet}, \quad (25)$$

$$dN_{\circ}/dt = 0. \quad (26)$$

These equations are integrated immediately; Eq. (26) gives

$$N_{\circ}(t) = N_{\circ}(0),$$

the initial amount of available sites; the insertion of this value into Eq. (25) gives a differential equation whose solution is straightforward,

$$N_{\bullet}(t) = \overline{N_{\bullet}} + [N_{\bullet}(0) - \overline{N_{\bullet}}] \exp(-Bt),$$

where $\overline{N_{\bullet}}$ is the equilibrium amount of filled sites,

$$\overline{N_{\bullet}} = (A/B)N_{\circ}(0).$$

The singular case will hereinafter be ignored.

2. Dynamics in the general case

Even the dynamics of the general case is better described in terms of ϵ and δ . For the reason given in Sec. III C, it is sufficient to limit the theory of adsorption on surfaces undergoing reconstruction $\mathcal{R}\langle A, B, \epsilon, \delta \rangle$ to its restriction to the case of reversible reconstruction $\mathcal{R}\langle A, B, \epsilon, 0 \rangle$:

$$dN_{\bullet}/dt = AN_{\circ} - BN_{\bullet}, \quad (27)$$

$$dN_{\circ}/dt = \epsilon(AN_{\circ} - BN_{\bullet}), \quad (28)$$

$$\epsilon = \epsilon(N_{\circ}, N_{\bullet}), \quad (29)$$

where the function $\epsilon(N_{\circ}, N_{\bullet})$ in Eq. (29) determines the kind of reconstruction. The special case $\mathcal{R}\langle A, B, -1, 0 \rangle$ generates the Langmuir theory $\mathcal{L}\langle A, B \rangle$; any function $\epsilon_{\mathcal{R}}(N_{\circ}, N_{\bullet})$, such that $\mathcal{R}\langle A, 0, \epsilon_{\mathcal{R}}(N_{\circ}, N_{\bullet}), 0 \rangle$ reproduces the Landsberg model, would provide an extension of the Langmuir theory able to include Landsberg's reconstruction mechanism.

D. The last restriction—the surface undergoes self-similar reconstruction

The intuitive notion of self-similar reconstruction seems to be captured by the following *self-similarity condition*: the net number of available sites generated per adsorption event, ϵ , is a function of the amount of available sites only, $\epsilon = \epsilon(N_{\circ})$.

The theory $\mathcal{S}\langle A, B, \epsilon(N_{\circ}) \rangle$ of adsorption on surfaces undergoing self-similar reversible reconstruction is therefore characterized by the following axioms:

(ASSRR 1) *one molecule per adsorption site. A site is filled by reaction with one and only one molecule; the extra-site space is unavailable for adsorption.*

(ASSRR 2) *absence of intermolecular interactions. Adsorbed molecules interact with each other neither laterally (along the surface) nor vertically (normally to the surface).*

(ASSRR 3) *surface homogeneity. All sites are equivalent.*

(ASSRR 4) *adsorption kinetics. The adsorption rate R_+ is proportional to the amount N_{\circ} of empty sites multiplied by the gas-phase flux Φ impinging onto the surface,*

$$R_+ = AN_{\circ}. \quad (30)$$

(ASSRR 5) *desorption kinetics. The desorption rate R_- is proportional to the amount N_\bullet of occupied sites,*

$$R_- = BN_\bullet. \quad (31)$$

(ASSRR 6) *gas ideality. The gas phase is ideal and described by the kinetic theory of gases.*

(ASSRR 7) *structureless adsorbate. The internal degrees of freedom of the molecule are not modified by adsorption, and adsorption is insensitive to them.*

(ASSRR 8) *self-similar reversible reconstruction. Adsorption results in the creation of α_+ empty sites per filled site, while desorption results in the formation of α_- per desorbed molecule; an adsorption-desorption cycle regenerates the original surface,*

$$\alpha_+ + \alpha_- = 1; \quad (32)$$

and the creation-destruction process is self-similar,

$$\alpha_+ - 1 = \epsilon(N_\circ). \quad (33)$$

It is emphasized that axioms ASSRR1, . . . , ASSRR7 coincide with (L1), . . . , (L7), respectively, the axiomatic system here described being different from Langmuir's one only for the possibility of describing surface reconstruction. In this way, $S\langle A, B, \epsilon(N_\circ) \rangle = \mathcal{R}\langle A, B, \epsilon(N_\circ), 0 \rangle$ and the unique free parameter added by $S\langle A, B, \epsilon(N_\circ) \rangle$ to $\mathcal{L}\langle A, B \rangle$ is the function $\epsilon(N_\circ)$. The basic equations which describe the considered dynamic system are given by Eqs. (27) and (28) with $\alpha_+ - 1$ specified by Eq. (33):

$$dN_\bullet/dt = AN_\circ - BN_\bullet, \quad (34)$$

$$dN_\circ/dt = \epsilon(N_\circ)(AN_\circ - BN_\bullet). \quad (35)$$

The goal of $S\langle A, B, \epsilon(N_\circ) \rangle$ is to demonstrate that situations of large practical and conceptual interest, not allowed in Langmuir theory, may instead be reproduced by simple specifications of $\epsilon(N_\circ)$ in Eq. (33), thus showing that the axiomatic system $\{\text{ASSRR1}, \dots, \text{ASSRR8}\}$ provides the basis for a genuine extension of the Langmuir theory to self-reconstructing surfaces.

Before developing the mathematical apparatus of the theory to deal with particular cases, we shall consider a property of $S\langle A, B, \epsilon(N_\circ) \rangle$ that holds true quite irrespective of the function $\epsilon(N_\circ)$. The time variation of the total number of sites is obtained summing side to side Eqs. (27) and (28):

$$d(N_\circ + N_\bullet)/dt = [1 + \epsilon(N_\circ)](AN_\circ - BN_\bullet). \quad (36)$$

Therefore, the total number of sites remains unchanged with time only at equilibrium (when $AN_\circ - BN_\bullet = 0$) or even in dynamic conditions when

$$\epsilon(N_\circ) = -1, \quad (37)$$

i.e., when $S\langle A, B, \epsilon(N_\circ) \rangle = S\langle A, B, -1 \rangle = \mathcal{L}\langle A, B \rangle$. This result shows that the constancy with time of the total amount of sites $N_\circ + N_\bullet$ is a peculiar property of the Langmuir theory alone.

E. The mathematical apparatus

Eliminating $AN_\circ - BN_\bullet$ between Eqs. (34) and (35), one gets

$$dN_\circ = \epsilon(N_\circ)dN_\bullet;$$

which is solved by separation of variables,

$$\int_{N_\circ^0}^{N_\circ} \frac{dN_\circ}{\epsilon(N_\circ)} = N_\bullet \quad (38)$$

with N_\circ^0 the amount of available sites at $N_\bullet = 0$ (N_\circ^0 must not be confused with the amount $N_\circ(0)$ of available sites at $t = 0$: $N_\circ^0 = N_\circ(0)$ only when $N_\bullet(0) = 0$). If $\epsilon(N_\circ)$ does not change sign, Eq. (38) can be solved for N_\circ , giving it as a function of N_\bullet ,

$$N_\circ = \eta(N_\bullet). \quad (39)$$

Substituting $\eta(N_\bullet)$ for N_\circ in Eq. (34) gives

$$dN_\bullet/dt = A\eta(N_\bullet) - BN_\bullet, \quad (40)$$

which is the key equation of the theory. In fact, the equilibrium condition is immediately obtained by putting $dN_\bullet/dt = 0$ therein,

$$\eta(N_\bullet) - (B/A)N_\bullet = 0, \quad (41)$$

while the kinetics are determined solving Eq. (40) by separation of variables,

$$\int_{N_\bullet(0)}^{N_\bullet(t)} \frac{dN_\bullet}{\eta(N_\bullet) - (B/A)N_\bullet} = At. \quad (42)$$

IV. THE CASE OF RECONSTRUCTION VARYING LINEARLY WITH THE DENSITY OF AVAILABLE SITES

The simplest case of the ASSRR theory is that of constant reconstruction: $\epsilon(N_\circ) = a = \text{constant}$. This case is of both conceptual and practical importance because it applies to a situation recently become of large interest—the growth of dendrimers [23]. Though this situation is formally allowed by the domain of ϵ [since ϵ is any function of N_\circ , $\epsilon(N_\circ)$ may be a constant], it however describes a reconstruction that is independent of the surface structure and will accordingly be ignored.

In order of increasing complexity, the second case to consider is that of a reconstruction varying linearly with the density of available sites,

$$\epsilon(N_\circ) = bN_\circ \quad (43)$$

that is expected to be able to reproduce the Landsberg behavior, at least in opportune conditions.

Inserting Eq. (43) into Eq. (38) gives

$$N_\circ = N_\circ^0 \exp(bN_\bullet). \quad (44)$$

The insertion of Eq. (44) into Eqs. (41) and (42) gives the equilibrium and kinetic equations, respectively, for the linear case,

$$N_{\circ}^0 \exp(bN_{\bullet}) = (B/A)N_{\bullet} \quad (45)$$

and

$$\int_{N_{\bullet}(0)}^{N_{\bullet}(t)} \frac{dN_{\bullet}}{N_{\circ}^0 \exp(bN_{\bullet}) - (B/A)N_{\bullet}} = At. \quad (46)$$

A. Equilibrium

We now write Eq. (45) in the form

$$e^{bN_{\bullet}} = \frac{B/A}{bN_{\circ}^0} bN_{\bullet} \quad (47)$$

and consider bN_{\bullet} as a variable and $(B/A)/bN_{\circ}^0$ as a parameter.

Assume first $b < 0$. In this case, Eq. (47) admits a unique negative solution bN_{\bullet} ; from $b < 0$ and $bN_{\bullet} < 0$, it follows that N_{\bullet} satisfies the physical condition of positiveness, $N_{\bullet} > 0$. Putting $B = 0$ should reproduce the same situation as considered by Landsberg so that the improper solution $bN_{\bullet} = -\infty$ (i.e., $N_{\bullet} = +\infty$), coinciding with the limit of $N_{\bullet}(t)$ for $t \rightarrow +\infty$ in the original Landsberg model, must be considered as a kind of equilibrium value of $N_{\bullet}(t)$; in this situation Eq. (44) gives $N_{\circ} = 0$.

Assume now $b > 0$. For $0 < B/AbN_{\circ}^0 < e$ (corresponding to the prevalence of adsorption and reconstruction over desorption), the dynamic system does not admit any equilibrium state. For $B/AbN_{\circ}^0 > e$, Eq. (47) admits two solutions N_{\bullet}^* and N_{\bullet}^{**} , which coincide for $B/AbN_{\circ}^0 = e$. Recognizing which (if any) of them is the equilibrium one will follow from the discussion of kinetics.

B. Kinetics

Understanding the kinetics requires the consideration of several cases.

1. The case $b < 0$

In this case, the system admits always one equilibrium state. The kinetics are different according to the occurrence that the initial condition $N_{\bullet}(0)$ is far from, or close to, the equilibrium value N_{\bullet} .

(a) *Behavior far from equilibrium.* The system may be far from equilibrium only in the early stages after its preparation. Its evolution will therefore be dominated either by adsorption [$N_{\circ}^0 e^{bN_{\bullet}} \gg (B/A)N_{\bullet}$] when $N_{\bullet}(0) \ll N_{\bullet}$, or by desorption [$N_{\circ}^0 e^{bN_{\bullet}} \ll (B/A)N_{\bullet}$] when $N_{\bullet}(0) \gg N_{\bullet}$.

If the evolution is dominated by adsorption, an integration of Eq. (46) gives

$$N_{\bullet}(t) - N_{\bullet}(0) \approx -\frac{1}{b} \ln(1 - N_{\circ}^0 e^{bN_{\bullet}(0)} bAt).$$

Remembering Eq. (44), one has

$$N_{\circ}(0) = N_{\circ}^0 \exp(bN_{\bullet}(0)),$$

so that, emphasizing that b is negative, the above kinetics become

$$N_{\bullet}(t) - N_{\bullet}(0) \approx \frac{1}{|b|} \ln(1 + |b|N_{\circ}(0)At)$$

that reproduce the ones originally proposed by Landsberg.

If the evolution is dominated by desorption, by integrating Eq. (46) one gets

$$N_{\bullet}(t) \approx N_{\bullet}(0) e^{-Bt},$$

for which the kinetics reduce to the ones of the Langmuir model.

(b) *Behavior close to equilibrium.* The region close to equilibrium is characterized by the condition $N_{\bullet}(t) \approx N_{\bullet}$; the behavior close to equilibrium can be studied treating the difference $\Delta N_{\bullet} := N_{\bullet}(t) - N_{\bullet}$ as a differential,

$$\begin{aligned} N_{\circ}^0 e^{bN_{\bullet}} - \frac{B}{A} N_{\bullet} &= N_{\circ}^0 e^{b(\overline{N_{\bullet}} + \Delta N_{\bullet})} - \frac{B}{A} (\overline{N_{\bullet}} + \Delta N_{\bullet}) \\ &\sim N_{\circ}^0 e^{b\overline{N_{\bullet}}} (1 + b\Delta N_{\bullet}) - \frac{B}{A} (\overline{N_{\bullet}} + \Delta N_{\bullet}) \\ &= \frac{B}{A} (\overline{N_{\bullet}} b - 1) \Delta N_{\bullet} \end{aligned} \quad (48)$$

because $N_{\circ}^0 e^{b\overline{N_{\bullet}}} - (B/A)\overline{N_{\bullet}} = 0$. Inserting Eq. (48) in Eq. (46) and integrating one has

$$\Delta N_{\bullet}(t) = \Delta N_{\bullet}(0) \exp(-B(1 + |b|\overline{N_{\bullet}})t).$$

2. The case $b > 0$

(a) *The system does not admit equilibrium states.* The dynamic system does not admit equilibrium states when

$$(N_{\circ}^0 \exp(bN_{\bullet})) > (B/A)N_{\bullet} \quad \forall N_{\bullet}.$$

Since $dN_{\bullet}/dt = N_{\circ}^0 \exp(bN_{\bullet}) - (B/A)N_{\bullet} > 0$, $N_{\bullet}(t)$ is an increasing function of t and

$$N_{\bullet} \rightarrow +\infty \Rightarrow N_{\circ}^0 \exp(bN_{\bullet}) - (B/A)N_{\bullet} \sim N_{\circ}^0 \exp(bN_{\bullet}).$$

Substituting $N_{\circ}^0 \exp(bN_{\bullet})$ for $N_{\circ}^0 \exp(bN_{\bullet}) - (B/A)N_{\bullet}$ in Eq. (46) and integrating one has

$$N_{\bullet}(t) - N_{\bullet}(0) \approx -\frac{1}{b} \ln[1 - bN_{\circ}(0)At]. \quad (49)$$

Since $b > 0$, this equation reproduces Cerofolini's extension of Landsberg's model.

(b) *The system admits one equilibrium state.* For $(B/A)/bN_{\circ}^0 > e$, Eq. (45) admits two solutions N_{\bullet}^* and N_{\bullet}^{**} (with $N_{\bullet}^* < N_{\bullet}^{**}$).

If $N_{\bullet}(0) > N_{\bullet}^{**}$, the system evolves running away to $+\infty$. To demonstrate this statement, observe that in this case the conditions $N_{\circ}^0 \exp(bN_{\bullet}) > (B/A)N_{\bullet}$ and $dN_{\bullet}/dt > 0$ hold true at $t=0$ and *a fortiori* for any positive t so that the solution of Eq. (46) increases steadily with time. Thus, even though Eq. (45) admits two positive roots, neither of them is actually attained by the system; rather the asymptotic behavior is obtained ignoring $(B/A)N_{\bullet}$ in Eq. (46). Once again the solution of the resulting equation has the expression (49) that reproduces Cerofolini's extension of Landsberg's model.

If $N_{\bullet}(0) < N_{\bullet}^{**}$, the system relaxes to the equilibrium value N_{\bullet}^* . This statement is demonstrated observing that $N_{\bullet}(t)$ decrease with t for $N_{\bullet}^* < N_{\bullet}(0) < N_{\bullet}^{**}$, while increases with t for $0 < N_{\bullet}(0) < N_{\bullet}^*$ that combined together make N_{\bullet}^* the equilibrium state of the system, $\overline{N_{\bullet}} = N_{\bullet}^*$. For N_{\bullet} in the vicinity of $\overline{N_{\bullet}}$, the system evolves with time as discussed in Sec. IV B 1 (b).

C. The case $\epsilon(N_{\circ}) = a - |b|N_{\circ}$

A particularly interesting situation results from the combination of dendritic growth with a reconstruction varying linearly with the amount of empty sites. For $b < 0$, this combination

$$\epsilon(N_{\circ}) = a - |b|N_{\circ} \quad (50)$$

is of particular interest because it may be used to model surface reconstruction dominated by dendritic growth in the early stages ($\epsilon \approx a$ for $N_{\circ} \ll a/|b|$) and eventually limited by a production of new sites linearly decreasing with N_{\circ} . In particular, Eq. (50) is expected to be able to describe multilayer adsorption on highly dispersed adsorbents, ini-

tially characterized by a dendritic growth of adsorption piles [12,13] and eventually limited by space filling [10].

Without considering the detailed mathematical analysis of this case (planned for another work), it is simply mentioned that the root of Eq. (50) (which according to the discussion of Sec. III B 2 determines $\overline{N_{\circ}} = a/|b|$ and $\overline{N_{\bullet}} = aA/|b|B$ as equilibrium state of the system) in general, is not a root of Eq. (41), thus providing a physically interesting example running in case (ii) of Sec. III B 2.

V. CONCLUSIONS

A theory has been formulated to incorporate the reconstruction phenomena occurring during adsorption and desorption within the Langmuir theory. The general formulation of the theory applies to both irreversible and reversible reconstruction.

A particular case of self-similar reversible reconstruction has been considered—the case of linear reconstruction. In this case, the behavior of the system is controlled by the value of the parameter b linking reconstruction to density of sites: For $b < 0$, the system admits always an equilibrium state; in this case and for negligible desorption rate the initial evolution of the system reduces to the kinetics originally predicted by Landsberg. For b small and positive, the system does not admit any equilibrium state and its kinetics are described by Cerofolini's extension of Landsberg model. For b large and positive, the system admits an equilibrium state, which is achieved or not in relation to the initial condition. When equilibrium is not achieved, the kinetics are once again described by Cerofolini's extension of Landsberg model.

-
- [1] I. Langmuir, *J. Am. Chem. Soc.* **40**, 1361 (1918).
 [2] W.A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon Press, Oxford, 1974).
 [3] G.F. Cerofolini and W. Rudziński, in *Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces*, edited by W. Rudziński, W.A. Steele, and G. Zgrablich (Elsevier, Amsterdam, 1997), p. 1.
 [4] G.A. Somorjai, in *The New Chemistry*, edited by N. Hall (Cambridge University Press, Cambridge, 2000), p. 137.
 [5] J. Monod, J. Wyman, and J.P. Changeux, *J. Mol. Biol.* **12**, 88 (1965).
 [6] G.F. Cerofolini and M. Cerofolini, *J. Colloid Interface Sci.* **78**, 65 (1980).
 [7] M. Pyda and M. Kurzyński, *Chem. Phys.* **67**, 7 (1982).
 [8] M. Pyda and M. Kurzyński, *Chem. Phys.* **79**, 219 (1983).
 [9] P.T. Landsberg, *J. Chem. Phys.* **23**, 1079 (1955).
 [10] G.F. Cerofolini, *Surf. Sci.* **366**, 597 (1996).
 [11] G.F. Cerofolini, *Langmuir* **13**, 995 (1997).
 [12] G.F. Cerofolini and L. Meda, *J. Colloid Interface Sci.* **202**, 104 (1998).
 [13] G.F. Cerofolini and L. Meda, *Surf. Sci.* **416**, 403 (1998).
 [14] S.Y. Elovich and G.M. Zhabrova, *Zh. Fiz. Khim.* **13**, 1761 (1939).
 [15] C. Aharoni and F.C. Tompkins, *Adv. Catal.* **21**, 1 (1970).
 [16] G.F. Cerofolini, in *Adsorption on New and Modified Inorganic Sorbents*, edited by A. Dabrowski and V.A. Tertykh (Elsevier, Amsterdam, 1995), Chap. 2.4, p. 435.
 [17] W. Rudziński and T. Panczyk, in *Surfaces of Nanoparticles and Porous Materials*, edited by J.A. Schwarz and C.I. Contescu (Marcel Dekker, New York, 1999), Chap. 15, p. 355.
 [18] G. Drazer and D.H. Zanette, *Phys. Rev. E* **60**, 5858 (1999).
 [19] M.O. Vlad, G.F. Cerofolini, and J. Ross, *Phys. Rev. E* **62**, 837 (2000).
 [20] P.T. Landsberg, *J. Appl. Phys.* **33**, 2251 (1962).
 [21] R.H. Austin, K.W. Beeson, L. Eisenstein, H. Frauenfelder, and I.C. Gunsalus, *Biochemistry* **14**, 5355 (1975).
 [22] W.G. Glöckle and T.F. Nonnenmacher, *Biophys. J.* **68**, 46 (1995).
 [23] G.R. Newkome, C.N. Moorefield, and F. Vögtl, *Dendrimers and Dendrons. Concepts, Syntheses, Applications* (Wiley-VCH, Weinheim, 2001).