Adsorption/Desorption Equilibria and Kinetics at Reconstructible Surfaces[†]

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ABSTRACT: A general kinetic theory, which takes explicit account of the phenomena occurring at reconstructible surfaces while adsorption or desorption proceed, is proposed. The theory contains a few free parameters which specify the adsorption and desorption rate constants, and the reconstruction and irreversibility degrees of the process.

INTRODUCTION

The adsorption of gases onto solid surfaces and their desorption (phenomena collectively referred to as AD-sorption – read as "a-d-sorption") may be described in a standard manner based on the hypothesis that adsorption produces the loss of a few translational degrees of freedom of gas-phase molecules (from 1, for mobile adsorption, to 3, for localized adsorption), leaving the internal partition function of the molecule and the structure of the surface otherwise unchanged. If this process occurs reversibly, desorption restores the pre-existing situation. The main characteristics of the theory of AD-sorption are thus structure-less molecules (hard adsorbates) and non-reconstructible surfaces (hard adsorbents) — the HH case in Figure 1. In many instances, the properties of an AD-sorption process are contained in its equilibrium isotherm (hereinafter simply called "isotherm") and in its AD-sorption kinetics.

The theory of AD-sorption was first formulated to describe localized sub-monolayer AD-sorption without lateral interactions on homogeneous surfaces and produced the Langmuir isotherm (Hill 1960; Steele 1974). The theory was later extended to account for lateral interactions, producing the Frumkin–Fowler–Guggenheim isotherm, or to describe mobile AD-sorption, producing the Hill–de Boer isotherm (Hill 1960). In the presence of lateral interactions, the theory predicted the possibility of two-dimensional condensation; experiments based on accurately prepared surfaces confirmed the existence of this phenomenon (Steele 1974). Other extensions were advanced to describe multilayer AD-sorption on homogeneous surfaces and produced the Brunauer– Emmett–Teller (BET) isotherm for approximately monolayer coverages or the Frenkel–Halsey–Hill isotherm at higher coverage (Steele 1974).

Consideration of the heterogeneous nature of the adsorbing surface was the subject of extended investigations that took place over many years (Cerofolini 1971, 1972, 1974, 1978; Rudziński and Jaroniec 1974; Jaroniec *et al*. 1976; Rudziński *et al*. 1982; Jaroniec and Bräuer 1986; Jaroniec and Madey 1988; Jagiello and Schwartz 1991; Rudziński and Everett 1992; Cerofolini and Re 1993; Cerofolini and Rudziński 1997); these investigations made it possible to explain surface heterogeneity in terms of numerous isotherms (such as those proposed by Freundlich, Temkin or Dubinin and Radushkevich), previously proposed empirically and known
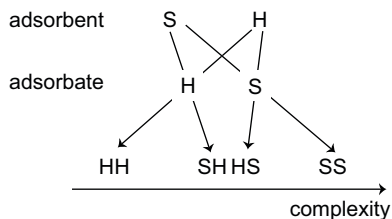
Figure 1. The complexity of AD-sorption phenomena in relation to the hard or soft nature of the adsorbent and the adsorbate.

to provide an accurate description of AD-sorption on real surfaces (Jaroniec 1975; Cerofolini 1975, 1976a,b, 1982, 1983).

For the description of heterogeneous surfaces, two major models were adopted: in one model the surface is visualized as being formed by a collection of indefinitely extended patches, each patch in itself being homogeneous (patch-wise heterogeneity), while in the other model each zone is formed, irrespective of its size, by a heterogeneous collection of sites with an adsorption-energy distribution independent of the size of the region (random heterogeneity). In the absence of lateral interactions, the two extreme topographies are equivalent. However, taking such interactions into account removes the equivalence; accounting for the involved correlation effects (Ripa and Zgrablich 1975) requires appropriate *ad hoc* constructions (Mayagoitia *et al*. 1990; Zgrablich *et al*. 1996a,b).

As a consequence, it was possible to formulate within the standard theory a scheme capable of describing even very difficult cases, such as AD-sorption onto fractal surfaces (Pfeifer and Avnir 1983; Avnir *et al*. 1983; Avnir and Jaroniec 1989; Pfeifer *et al*. 1989; Jaroniec1995; Pfeifer and Liu 1997) or onto surfaces where geometric heterogeneity is combined with energetic heterogeneity (Rudziński *et al*. 2001). For several AD-sorption models, time evolution of the system (described using ordinary rate equations with integral order exponents) was found to produce equilibrium states consistent, if not exactly the same, with those predicted by statistical mechanics.

Although the above development occurred in a time span of approximately one century (the entire 20th century), the HH case depicted in Figure 1 applies only to situations where the adsorption energy is small compared to the energy of other internal configurations of the surface and molecule — that may happen only for van der Waals adsorption forces. The HH case, restricting the theory to physisorption, does not exhaust the complexity of AD-sorption phenomena. In fact, whereas AD-sorption-induced surface reconstruction, protein denaturation upon adsorption on polar surfaces, or antigen–antibody interaction, etc., appear as genuine AD-sorption phenomena, they do not fit the HH case. In these cases, the adsorbate, adsorbent, or both undergo even large changes in their internal partition functions during the process and must thus be viewed as soft.

With respect to reconstruction, Figure 1 shows that there are four possible cases: HH, hard adsorbent and hard adsorbate; SH, soft adsorbent and hard adsorbate; HS, hard adsorbent and soft adsorbent; and SS, soft adsorbent and soft adsorbate. Their complexity increases from case HH to case SS. In this work, the standard theory of AD-sorption will be extended to account for the AD-sorption on soft surfaces of hard adsorbates — the SH case.

AD-SORPTION ON HARD SURFACES

The construction of the theory of AD-sorption is usually assumed to go back to the second decade of the 20th Century, when Langmuir gave a kinetic description of adsorption and desorption

assuming that they are first-order processes in the available and occupied sites, respectively, and the processes run leaving unchanged the total amount of (empty or full) adsorption sites (Langmuir 1918). The elementary development of the theory is reported here essentially with the aim of defining symbols. In the above hypotheses, the amount N of adsorbed molecules and site coverage Θ are simply proportional,

$$N = N_m \Theta \tag{1}$$

(with N_m being the total amount of sites) and the rate equations are given by

$$dN_m/dt = 0 \tag{2}$$

$$d\Theta/dt = A(1 - \Theta) - B\Theta \tag{3}$$

where A and B are the rate constants for adsorption and desorption, respectively. The solution of equations (2) and (3) is trivial:

$$N_m = \text{constant} \tag{4}$$

$$\Theta(t) = \overline{\Theta} + \left(\Theta(0) - \overline{\Theta}\right) \exp\left(-t/\tau_L\right) \tag{5}$$

where τ_L is the harmonic composition of the time constants A^{-1} and B^{-1}

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

$\Theta(0)$ is the initial condition, and $\overline{\Theta}$ is given by

$$\overline{\Theta} = \left(B/A + 1\right)^{-1} \tag{6}$$

The kinetic theory of gases and the absolute rate theory specify A and B as follows:

$$A = \sigma p / \sqrt{2\pi m k_B T} \tag{7}$$

$$B = \nu \exp\left(-E^*/k_B T\right) \tag{8}$$

with σ being the cross-section for the (possibly activated) gas adsorption on each surface site, p the partial pressure of the gas, T the temperature, k_B the Boltzmann constant, m the molecular mass, ν the vibration frequency perpendicular to the surface, and E^* the activation energy for desorption (coinciding in the simple cases with the adsorption energy q). In terms of these quantities, the combination of equations (1) and (6) gives the familiar expression of the Langmuir isotherm:

$$\overline{N} = N_m \left(\frac{(\nu/\sigma)\sqrt{2\pi m k_B T}}{p} \exp\left(-\frac{E^*}{k_B T}\right) + 1\right)^{-1} \tag{9}$$

For the Langmuir model, a statistical mechanical derivation is known. It is obtained by considering the number of configurations of N distinguishable particles in N_m identical sites with an adsorption energy q; the statistical mechanical derivation then gives

$$\overline{N} = N_m\left(\frac{p_L}{p}\exp\left(-\frac{q}{k_B T}\right) + 1\right)^{-1} \tag{10}$$

where $p_L = p_0/z$, $p_0 = k_B T(2\pi m k_B T/h^2)^{3/2}$, h is the Planck constant, and z is the internal partition function of the underlined adsorbed molecule. Thus, equations (9) and (10) coincide provided that $q = E^*$ and $p_L = (\nu/\sigma)\sqrt{2\pi m k_B T}$ or equivalently

$$\frac{p_L}{p}\exp\left(-\frac{q}{k_B T}\right) = \frac{B}{A} \tag{11}$$

AD-SORPTION ON SOFT SURFACES

Any theory $\mathcal{T}$ extending the Langmuir theory to AD-sorption on surfaces undergoing reconstruction should satisfy the following features:

1. $\mathcal{T}$ is constructed on the basis of the mass-action law;
2. $\mathcal{T}$ is reduced to the Langmuir theory in the absence of reconstruction; and
3. the equilibrium AD-sorption isotherm obtained from the kinetic model can be recovered (at least in particular cases) from statistical mechanics.

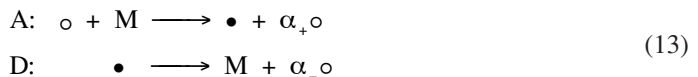As shown in the following, to some extent this goal is possible.

For the construction of $\mathcal{T}$ the hypotheses underlying the Langmuir theory will be re-written in the following scheme (Cerofolini 2003a,b):

$$\begin{aligned} \text{A:} \quad \circ + M &\longrightarrow \bullet \\ \text{D:} \quad \bullet &\longrightarrow M + \circ \end{aligned} \tag{12}$$

where $\circ$ denotes an empty site, M a molecule, and $\bullet$ a site filled with one molecule M. Since, in theory, a site is either empty or occupied (and no other state is possible), the total amount of sites is given by $N_\circ + N_\bullet$.

The constancy of $N_\circ + N_\bullet$ in the Langmuir theory follows from the following facts: the disappearance of one empty site after adsorption results in the birth of one filled site, vice versa for desorption, and at equilibrium each adsorption event is on average followed by a desorption event.

Dynamic systems with surface reconstruction, once considered as reactions involving empty and filled sites are, in general, not described by reactions (12). Rather,

$$\begin{aligned} \text{A:} \quad \circ + M &\longrightarrow \bullet + \alpha_+\circ \\ \text{D:} \quad \bullet &\longrightarrow M + \alpha_-\circ \end{aligned} \tag{13}$$

(where the stoichiometric coefficients α_+ and α_- are free parameters of the theory) seems to provide a sufficiently general, but still tractable, scheme for the description of AD-sorption on reconstructible surfaces.

The idea underlying reaction scheme (13) is geometric in character — depending on the values of α_+ and α_- , AD-sorption-induced reconstruction is responsible for roughening or smoothing of the surface. However, any geometric change in the surface is responsible for changes in the energy landscape of the system too, increasing or decreasing the energy heterogeneity of the surface. Roughening without heterogenization as well as smoothing without homogenization are both indeed improbable phenomena unless the energy landscape of the system is very smooth. Examples of processes that may be described by reaction scheme (13), dominated by geometric rather than energetic factors, may thus be the following:

- reactions at porous oxides by hydrolysis of oxo bridges produced by water physisorbed onto hydroxyl terminations (A) and the condensation with elimination of water from nearby hydroxyl groups (D), or
- the unfolding (A) and folding (D) of proteins resulting from AD-sorption of water or other polar molecules.

In the opposite approach, the geometric changes occurring during AD-sorption are described only in terms of the heterogenization of the surface. The corresponding treatment of this case is represented by the Monod–Wyman–Changeux treatment of allosteric effects(Monod *et al*. 1965).

The author is aware of one attempt only for the analytical description of the geometric and energetic changes simultaneously resulting during AD-sorption (Cerofolini and Cerofolini 1980); this matter still seems too difficult for quantitative modelling.

Since, in an AD-sorption cycle described by reaction scheme (13), the numbers of molecules and filled sites remain unchanged while the total number of empty sites varies by an amount $\alpha_+ + \alpha_- - 1$, the surface undergoes a *reversible* reconstruction when

$$\alpha_+ + \alpha_- = 1 \tag{14}$$

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

The rate equations for reaction scheme (13) are given by

$$\frac{dN_\bullet}{dt} = AN_\circ - BN_\bullet \tag{15}$$

$$\frac{dN_\circ}{dt} = (\alpha_+ - 1)AN_\circ + \alpha_- BN_\bullet \tag{16}$$

where A and B maintain the same meaning as in equations (7) and (8).

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

$$0 = AN_\circ - BN_\bullet \tag{17}$$

$$0 = (\alpha_+ - 1)AN_\circ + \alpha_- BN_\bullet \tag{18}$$

involves at least a non-trivial solution $\left(\overline{N}_\circ, \overline{N}_\bullet\right)$, in addition to the trivial solution (0, 0).

In the search for equilibrium states, equation (17) should first be solved for $N_\bullet, N_\bullet = AN_\circ/B$; the insertion of this result into equation (18) gives

$$\left[(\alpha_+ - 1) + \alpha_-\right]AN_\circ = 0$$

that is satisfied for $AN_\circ = 0$ (the trivial case), or for α_+ and α_- satisfying equation (14): the necessary condition for the occurrence of equilibrium is that the AD-sorption process is reversible.

The corresponding equations describing the time evolution of the system when equation (14) is not satisfied may be written as a function of the degree of irreversibility of the AD-sorption process as follows. Let ε be the net number of empty sites generated per adsorption event

$$\varepsilon = \alpha_+ - 1$$

(ε is a kind of *degree of reconstruction* of the surface) and let δ be the net number of empty sites produced in an AD-sorption cycle per newly formed site, where

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

Since for reversible AD-sorption $\delta = 0$, δ may be considered as a kind of *degree of irreversibility* of the process. In terms of ε and δ, equations (15) and (16) become

$$dN_\bullet/dt = AN_\circ - BN_\bullet \tag{19}$$

$$dN_\circ/dt = \varepsilon\left[AN_\circ - (1 - \delta)BN_\bullet\right] \tag{20}$$

In terms of ε and δ, equilibrium is specified by the conditions

$$0 = AN_\circ - BN_\bullet \tag{21}$$

$$0 = \varepsilon\left[AN_\circ - (1 - \delta)BN_\bullet\right] \tag{22}$$

Equations (21) and (22) are mutually consistent only if δ is equal to zero. In the following, the discussion will be limited to the case of reversible reconstruction:

$$\forall N_\circ, N_\bullet\left[\delta(N_\circ, N_\bullet) = 0\right]$$

If $\delta = 0$, equations (21) and (22) give consistent equilibrium conditions irrespective of any possible dependence of ε on $N_\circ$ and $N_\bullet$ (although the occurrence or not of equilibrium may depend on the initial condition). The determination of the kinetics, instead, requires that such a dependence,

$$\varepsilon = \varepsilon(N_\circ, N_\bullet) \tag{23}$$

is specified. With respect to the dependence of ε on both $N_\circ$ and $N_\bullet$, nothing can be said in general; however, if $\varepsilon(N_\circ, N_\bullet) \neq 0$, dividing equations (20) and (19) member by member leads to the following differential equation

$$dN_\circ/dN_\bullet = \varepsilon(N_\circ, N_\bullet) \tag{24}$$

If ε depends on either N_o or $N_\bullet$, equation (24) can be solved by the separation of the variables, and the solution allows the dynamic system {(15), (16), (23)} to be integrated by reduction to quadratures. The discussion in the Appendix to this paper deals with the case of ε depending on N_o alone.

The reason why the dynamic system (13) is referred to as a "reaction system" rather than as a "reaction" arises from the fact that α_+ and α_- are, in general, dependent on N_o and $N_\bullet$, and that different dependencies may describe qualitatively different physical situations. Attention was initially focused on the case of reversible AD-sorption, described by equation (14), and on $\varepsilon(N_o, N_\bullet)$ depending linearly on N_o only (Cerofolini 2003a,b). This choice provided an extension of the model originally proposed by Landsberg to account for the Elovich equation in adsorption kinetics (Landsberg 1955, 1962). A brief treatment of this case is given in the Appendix to this paper.

In the present paper, the dynamic system will be developed for the case of ε being independent of N_o and $N_\bullet$:

$$\varepsilon(N_o, N_\bullet) = \varepsilon_0 = \quad \text{constant} \tag{25}$$

Although this case is simpler than the one described in the Appendix, it is formally interesting and provides a model for γ-on statistics.

AD-SORPTION WITH A CONSTANT DEGREE OF RECONSTRUCTION

Equation (25) is the simplest case described by reaction system (13), namely constant reconstruction. According to the sign of ε_0, adsorption may result in progressive passivation of the original sites ($\varepsilon_0 < 0$) or in growth ($\varepsilon_0 > 0$). The case of constant reconstruction with $\varepsilon_0 > 0$ applies to a situation which has recently acquired considerable interest — the growth of dendrimers (Newkome *et al*. 2001).

Before confining the analysis to equilibrium situations, it may be observed that for $\varepsilon_0 \neq 0$, equation (24) becomes

$$dN_o/dN_\bullet = \varepsilon_0$$

whose integration is straightforward:

$$N_o = N_o^0 + \varepsilon_0 N_\bullet \tag{26}$$

with N_o^0 being the amount of empty sites in the absence of adsorbed particles. Equation (26) holds true even for $\varepsilon_0 = 0$ and therefore holds true for all ε_0 values (note that for $\varepsilon_0 = -1$ it reduces to $N_o + N_\bullet = N_o^0$, giving the constancy of the number of sites, irrespective of their degree of occupation).

Equilibrium

Inserting equation (26) into the other equilibrium condition, equation (21), leads to an equation that provides a unique physical solution $\overline{N_\bullet}$ (with $\overline{N_\bullet} > 0$) only for $\varepsilon_0 < B/A$:

$$\overline{N_\bullet} = N_o^0\left(B/A - \varepsilon_0\right)^{-1} \tag{27}$$

$$\overline{N_o} = N_o^0\left(1 - \varepsilon_0 A/B\right)^{-1} \tag{28}$$

Summing equations (27) and (28) side by side gives

$$\overline{N_{\circ}} + \overline{N_{\bullet}} = N_{\circ}^{0}\left(1 + \frac{1 + \varepsilon_0}{B/A - \varepsilon_0}\right)$$

from which the Langmuir theory is once again reproduced ($\overline{N_{\circ}} + \overline{N_{\bullet}} = N_{\circ}^{0}$) for $\varepsilon_0 = -1$.

Bearing equation (11) in mind, equation (27) becomes

$$\overline{N_{\bullet}}/N_{\circ}^{0} = \frac{1}{\left(p_{L}/p\right)\exp\left(-q/k_{B}T\right) - \varepsilon_0} \tag{29}$$

For $\varepsilon_0 = -1$, this isotherm is reduced to the Langmuir isotherm provided that $N_{\circ}^{0} = N_{m}$.

Taking $\varepsilon_0 = 1$, $q = q_s$ (the latent heat of evaporation from the bulk phase) and $p_L\exp(-q_s/k_BT) = p_s$ (the saturated vapour pressure at temperature T), equation (29) may be used instead to describe AD-sorption in multilayers:

$$\overline{N_{\bullet}}/N_{\circ}^{0} = x/(1 - x) \tag{30}$$

where x is the relative pressure, $x = p/p_s$. In terms of relative pressure, the Langmuir isotherm may be written as $\Theta = Cx/(1 + Cx)$ with $C = \exp\left[(q - q_s)/k_BT\right]$. Multilayer AD-sorption on the top of a layer directly adsorbed on the surface and obeying the Langmuir isotherm is thus described by the equation

$$\overline{N_{\bullet}}/N_{\circ}^{0} = \overbrace{\frac{Cx}{1 + Cx}}^{\text{bound to the surface}} + \frac{Cx}{1 + Cx}\overbrace{\frac{x}{1 - x}}^{\text{in multilayers}}$$
$$= \frac{1}{1 - x}\frac{Cx}{1 + Cx} \tag{31}$$

Provided that $C \gg 1$ (as is usually the case), equation (31) is almost indistinguishable from the original BET equation,

$$\overline{N_{\bullet}}/N_{\circ}^{0} = \frac{1}{1 - x}\frac{Cx}{1 + (C - 1)x}$$

Time evolution

Inserting equation (26) into equation (19) gives

$$\int_{N_{\bullet}(0)}^{N_{\bullet}(t)} \frac{dN_{\bullet}}{N_{\circ}^{0} - \left(B/A - \varepsilon_0\right)N_{\bullet}} = At$$

whose integration is elementary:

$$\ln\left(\frac{1 - \left(B/A - \varepsilon_0\right)N_\bullet(t)/N_\circ^0}{1 - \left(B/A - \varepsilon_0\right)N_\bullet(0)/N_\circ^0}\right) = -A\left(B/A - \varepsilon_0\right)t \tag{32}$$

Defining

$$\tau_{\varepsilon_0}^{-1} := A\left(B/A - \varepsilon_0\right) = B - \varepsilon_0 A$$

and recalling equation (27), equation (32) becomes

$$N_\bullet(t) = \overline{N_\bullet} + \left(N_\bullet(0) - \overline{N_\bullet}\right)\exp\left(-t/\tau_{\varepsilon_0}\right) \tag{33}$$

The kinetics are therefore controlled by the sign of $B/A - \varepsilon_0$: for $B/A - \varepsilon_0 > 0$, the amount of filled sites relaxes to the equilibrium value with an exponential decrease of the initial algebraic excess; otherwise, for $B/A - \varepsilon_0 < 0$, the solution runs away diverging exponentially (with upward concavity) to $+\infty$ with a time constant $\left|A(B/A - \varepsilon_0)\right|$. The behaviour described by equation (33) for the first case, i.e. exponential relaxation to equilibrium, is similar to what happens for the Langmuir isotherm; what changes is simply the time constant of the process.

AD-SORPTION ON RECONSTRUCTIBLE SURFACES AS A MODEL FOR γ-ON STATISTICS

Let us consider a system with a chemical potential μ obtained by arranging N non-interacting particles in M equivalent sites. If f denotes the mean occupation number of the energy level E, the formula

$$f = \left[\exp\left(\frac{E - \mu}{k_B T}\right) + \gamma\right]^{-1} \tag{34}$$

converts to the canonic Fermi–Dirac, Bose–Einstein or Boltzmann occupation statistics for γ values of $+1$, -1, or 0.

Relationship (34) may formally be regarded as the occupation statistics of a class of particles (called *γ-ons*) whose statistical properties may be deduced by assuming that N particles can be arranged in M states in a number W(N) of ways given by

$$W(N) = \frac{1}{N!}\left(\frac{M!}{(M - \gamma N)!}\right)^{1/\gamma} \tag{35}$$

with $\gamma \neq 0$; the singular case $\gamma = 0$ requires special analysis as described by Byczuk *et al*. (1995). To date, a physical derivation of equation (35) has not been advanced (Acharya and Swamy 1994).

We now return to equilibrium AD-sorption on reconstructible surfaces with constant reconstruction. Defining $Q = -k_B T \ln(p/p_L)$, equation (10) takes the form

$$\frac{\overline{N}}{N_o^0} = \left(\exp\left(\frac{Q - q}{k_B T} \right) - \varepsilon_0 \right)^{-1} \tag{36}$$

Interpreting Q as an energy level, q as chemical potential and ε_0 as $-\gamma$, not only does equation (36) coincide (for $N = N_\bullet$ and $M = N_o^0$) with equation (34) and reproduce the canonic occupation statistics for suitable values of ε_0, but it also *provides a concrete example of γ-on statistics*.

This fact is quite surprising because at a first glance one could be tempted to assume that the statistical mechanics of equilibrium AD-sorption on reconstructible surfaces is described by Haldane fractional statistics (Haldane 1991). Consider a box formed by M sites that can be filled by structure-less particles. Assuming that the number of available states N_o after the adsorption of N particles is given by $N_o = M + N(\alpha - 1)$ [with α constant with N and having the same meaning as α_+ in reaction scheme (13)], and using the familiar counting statistics:

$$W(N) = \frac{(N_o + N - 1)!}{N!(N_o - 1)!}$$

instead of (34), one gets the occupation statistics of *anyons* (Haldane 1991):

$$\exp\left(\frac{\mu - E}{k_B T} \right) = \frac{f}{(1 + \alpha f)^\alpha \left[1 - (1 - \alpha)f \right]^{1 - \alpha}} \tag{37}$$

where $f = N/M$. Equation (37) does not coincide with (34), so that the counting statistics (35) is not recovered in the frame of Haldane fractional statistics; however, it should be noted that in the high-temperature limit equation (37) is reduced to (34) (Byczuk *et al.* 1995) and hence to (29).

Haldane fractional statistics were first considered in AD-sorption phenomena by Riccardo and co-workers (Riccardo *et al.* 2004; Romá *et al.* 2006), who applied their analysis to the case of AD-sorption of polyatomic molecules where the adsorption of one molecule depresses more sites than the one actually occupied; the general case considered above and extending even beyond the usual limits $(-1, +1)$ was instead treated by Cerofolini (2006).

MATHEMATICS, AT LAST

The "unreasonable effectiveness of mathematics in the natural sciences" (i.e., that the mathematical structure of a physical theory often points the way to further advances in that theory and even to empirical predictions) led Wigner to argue that this is not just a coincidence and should therefore reflect some larger and deeper truth about both mathematics and physics (Wigner 1960).

Without pretending to give exhaustive answers to the puzzle of the miracle of the appropriateness of the language of mathematics for the formulation of the laws of natural sciences (Wigner 1960; Colyvan 2001), it is suggested that one of the reasons for such an *unreasonable effectiveness* is that the application

$$\text{mathematics} \longrightarrow \text{natural sciences}$$

can, to some extent, be inverted (in a way that it may thus be considered injective). For example, in the preface to his book entitled *Thermodynamics and Statistical Mechanics*, Landsberg (1978) mentioned several points of interest for those who are fascinated by the interaction between physics and mathematics: how thermodynamics is related to the theorem that the arithmetic mean of two numbers is less than the geometric mean, how the increase in entropy can be described in terms of the notion of equivalence classes and how the Euler formula concerning the vertices, edges and faces of a convex polyhedron can be related to the Gibbs' phase rule. Since the author shares this fascination, it is intended to close this paper by discussing how the theory of AD-sorption on reconstructing surfaces as given here may be formulated to extend to one of the most fundamental concepts of mathematics — the natural numbers.

The theory of AD-sorption on reconstructing surfaces can formally be re-stated by considering a system S admitting a set of states S_n (n being a natural number, $n \in \mathbb{N}$) such that each state has internal degrees of freedom (empty states, $\circ$, and filled states, $\bullet$) and evolves via exchange with its environment of ambient particles M ('tokens') according to the following processes:

$$A_{\alpha_+}: \quad \circ + M \longrightarrow \bullet + \alpha_+ \circ$$
$$D_{\alpha_-}: \quad \bullet \longrightarrow \alpha_- \circ + M \tag{38}$$
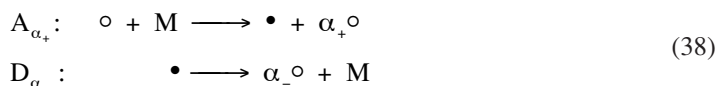
where α_+ and α_- are real numbers ($\alpha_+, \alpha_- \in \mathbb{R}$) independent of the state S_n.

Assuming that the states S_n can undergo both A_{α_+} and D_{α_-} processes,

$$A_{\alpha_+} S_n = S_{n+1}$$
$$D_{\alpha_-} S_n = S_{n-1}$$

in general, one has that $D_{\alpha_-} A_{\alpha_+} S_n \neq S_n$. Actually, condition $D_{\alpha_-} A_{\alpha_+} S_n \neq S_n$ is only possible for reversible processes. For them, the following relationship holds true:
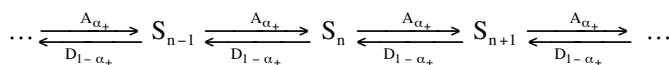
$$\forall n D_{1 - \alpha_+} A_{a_+} S_n = S_n$$

This relationship states that considering A_{α_+} and D_{α_-} as operators acting on S_n, D_{α_-} can be considered as the inverse $A_{\alpha_+}^{-1}$ of A_{α_+} if $\alpha_+ + \alpha_- = 1$:

$$A_{\alpha_+}^{-1} = D_{1 - \alpha_+}$$

(and *mutatis mutandis* similarly for $D_{\alpha_-}^{-1}$). Limiting the attention to the case of reversible AD-sorption, the operators A_{α_+} and $D_{1 - \alpha_+}$ may be viewed as ladder operators:

$$A_{\alpha_+} S_n = S_{n+1}$$
$$D_{1 - \alpha_+} S_n = S_{n-1}$$

The discrete states $\{S_n\}$ and processes A_{α_+} and $D_{1 - \alpha_+}$ thus form a Markov chain:

$$\cdots \underset{D_{1-\alpha_+}}{\overset{A_{\alpha_+}}{\rightleftarrows}} S_{n-1} \underset{D_{1-\alpha_+}}{\overset{A_{\alpha_+}}{\rightleftarrows}} S_n \underset{D_{1-\alpha_+}}{\overset{A_{\alpha_+}}{\rightleftarrows}} S_{n+1} \underset{D_{1-\alpha_+}}{\overset{A_{\alpha_+}}{\rightleftarrows}} \cdots$$

The underlying physical processes used to generate such a chain are now ignored, it being considered as given axiomatically. No assumption is made as to whether the Markov chain has a lower bound $\underline{n}$ (that would imply the existence of a state $S_{\underline{n}}$ such that $D_{1-\alpha_+}S_{\underline{n}}$ is not defined) or an upper bound (that would imply the existence of a state $S_{\bar{n}}$ such that $A_{\alpha_+}S_{\bar{n}}$ is not defined).

If $\underline{n}$ is finite, without loss of generality it can be taken as 0 and this case can be used to model reversible AD-sorption; instead, if $\underline{n} = -\infty$, the Markov chain (39) can be used to model the evaporation/condensation equilibrium at liquid surfaces. A finite value for $\bar{n}$ implies instead that AD-sorption occurs in a restricted geometry (thereby placing a limit on the thickness of the adsorbed film) or is completed with total passivation of the adsorbed film, while $\bar{n} = +\infty$ implies the absence of such effects.

Let us now relax the condition of reversibility,

$$\alpha_- \neq 1 - \alpha_+ \tag{40}$$

In the case of irreversibility, the repeated application of the same operator A_{α_+} to any S_n generates an ascending sequence of states: from S_0 to $S_1 \left(= A_{\alpha_+}S_0\right)$, $S_2 \left(= A_{\alpha_+}S_1 = A_{\alpha_+}^2 S_0\right)$, and so on. The application of an operator D_{α_-} to S_n however generates a state S'_{n-1} that does not coincide with S_{n-1}. Similarly, the application of a descending operator to any of the states S'_m does not yield the state S'_{m-1} (generating S'_m by the application of A_{α_+}) but still another state S''_{m-1}. In this way, the overall AD-sorption process may be viewed as a hierarchy of ascending Markov chains, each generated from a descending state, as sketched in Figure 2.

Leaving aside the complexity of irreversible AD-sorption for a moment, let us concentrate on the possibility of using reaction scheme (38) for the definition of a new class of mathematical quantities that generalize the concept of natural numbers.

As discussed by Fraenkel (1955), natural numbers embody two properties in themselves: they are ordinals (as they are capable of ordering sequentially all elements created by a certain process) and they are also cardinals (as they quantify the content of any finite set). What is special in natural numbers is that these properties — so different in principle — actually coincide. On other hand, it would be interesting to construct a set $\mathbb{N}_C$ depending on a set of parameters C reducing to $\mathbb{N}$ for suitable values of the parameter, but otherwise able to distinguish order from content.
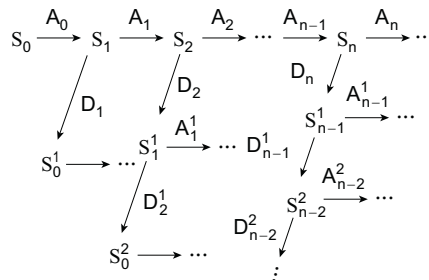
Figure 2. The intricate Markov chain describing irreversible AD-sorption.

Before trying to construct $\mathbb{N}_C$, let us recall the Peano axioms for natural numbers:

P 1 *If n is a natural number, the successor n' of n is a natural number.*
P 2 *There is a natural number, called 0, that is not a successor of any natural number.*
P 3 *If m' = n', then m = n.*
P 4 (**Principle of Induction**) *Let S be a set containing 0; then, if for all n in S, n' is also in S, then S coincides with $\mathbb{N}$.*

Thus, the Peano scheme is essentially defined by two characters — numbers and the operation that generates a successor from any given number. Since n repetitions of the same unit operation generate a set with just n objects, the Peano axioms imply the equivalence between ordinality and cardinality.

Reaction scheme (38) contains three elements, viz. empty sites ($\circ$), filled sites ($\bullet$) and a unit operation ($+M$); in this way it contains sufficient elements to map ordinality (sequence of operations) and cardinality (content) differently.

Define the operation of filling the pre-existing void sites as the *complete adsorption event* and consider first the case of reversible AD-sorption. Imagine starting from a situation where the system is formed by only one empty site. The first complete adsorption event (i.e. the filling of the original site by one molecule) produces α_+ empty sites. The second complete adsorption event (i.e. the filling of the newly generated α_+ sites with α_+ molecules) produces two empty sites and the system contains $1 + \alpha_+$ molecules. Repeating the argument, the system after the nth complete adsorption event will be formed by α_+^n empty sites and will contain $1 + \alpha_+ + \alpha_+^2 + \cdots + \alpha_+^{n-1}$ molecules.

To simplify the notation, let us denote α_+ by α. Let $\mathfrak{n}_\alpha$ be the ordered pair given by the progressive order of adsorption n and the amount of tokens $s_n(\alpha)$ contained in the system,

$$\mathfrak{n}_\alpha = (n, s_n(\alpha))$$

where $\mathfrak{n}_\alpha$ depends on α because of the dependence of s_n on α: $s_n(\alpha) = 1 + \alpha_1 + \alpha^2 + \cdots + \alpha^{n-1}$;

$s_n(\alpha) = \left(1 - \alpha^n\right)/\left(1 - \alpha\right)$ for $\alpha \neq 1$, or $s_n(\alpha) = n$ for $\alpha = 1$.

Let $\mathbb{S}_\alpha$ be the set of all $\mathfrak{n}_\alpha$ and denote with $\mathscr{A}_\alpha$ the operation bringing $\mathfrak{n}_\alpha$ onto $(\mathfrak{n} + 1)_\alpha$:

$$\mathscr{A}_\alpha \mathfrak{n}_\alpha = ((\mathfrak{n} + 1), s_{n+1}(\alpha))$$
$$= (\mathfrak{n} + 1)_\alpha$$

In view of this definition, the following properties hold true:

Property 1 *If $\mathfrak{n}_\alpha$ is a member of $\mathbb{S}_\alpha$, $(\mathfrak{n} + 1)_\alpha$ belongs to $\mathbb{S}_\alpha$.*
Property 2 *The element $\mathbb{O}_\alpha$ cannot be obtained by the application of $\mathscr{A}_\alpha$ to any member $\mathfrak{n}_\alpha$ of $\mathbb{S}_\alpha$.*
Property 3 *If $\mathscr{A}_\alpha \mathfrak{n}_\alpha = \mathscr{A}_\alpha \mathfrak{m}_\alpha$, then $\mathfrak{n}_\alpha = \mathfrak{m}_\alpha$.*
Property 4 *If $\mathbb{O}_\alpha \in \mathbb{S}_\alpha$ and if, for any $\mathfrak{n}_\alpha \in \mathbb{S}_\alpha$, $\mathscr{A}_\alpha \mathfrak{n}_\alpha \in \mathbb{S}_\alpha$ also applies, then the sequence $\{\mathbb{O}_\alpha, \mathscr{A}_\alpha \mathbb{O}_\alpha, \mathscr{A}_\alpha^2 \mathbb{O}_\alpha, \mathscr{A}_\alpha^3 \mathbb{O}_\alpha,...\}$ exhausts $\mathbb{S}_\alpha$.*

From these properties one can define

- an **ordering**, which states that $\mathfrak{m}_\alpha < \mathfrak{n}_\alpha$ if $\mathfrak{n}_\alpha$ is obtained by the application, possibly repeated, of $\mathscr{A}_\alpha$ to $\mathfrak{m}_\alpha$ and,

- an **addition**, defining $\mathfrak{m}_\alpha + \mathfrak{n}_\alpha$, and
- a **subtraction**, defining, for $\mathfrak{n}_\alpha > 0_\alpha$, $(\mathfrak{n} - 1)_\alpha$ in terms of a descending operator $D_{1-\alpha}$,

$$(\mathfrak{n} - 1)_\alpha = D_{1-\alpha}\mathfrak{n}_\alpha = (n - 1, s_{n-1}(\alpha))$$

and re-iterating the procedure to all $\mathfrak{m}_\alpha$, with $\mathfrak{m}_\alpha \leq \mathfrak{n}_\alpha$

$$(\mathfrak{n} - \mathfrak{m})_\alpha = D_{1-\alpha}^m \mathfrak{n}_\alpha = (n - m, s_{n-m}(\alpha))$$

It is straightforward to verify that relation and operations maintain the same properties as for natural numbers.

Thus, provided that $\mathscr{H}_\alpha$ is interpreted as the operation of taking the successor in Peano axioms and the states of the AD-sorption system are identified with the natural numbers, the above properties are the same as for natural numbers, thereby allowing the set of all $\mathfrak{n}_\alpha$ to be denoted as $\mathbb{N}_\alpha$:

$$\mathbb{N}_\alpha = \{0_\alpha, 1_\alpha, 2_\alpha, \ldots, \mathfrak{n}_\alpha, \ldots\}$$

However, an important fact should be noted: the elements n and $s_n(\alpha)$ (denoting the ordinality and cardinality, respectively, of n_α) generally do not coincide. As a consequence, each $\mathbb{N}_\alpha$ can be taken as a model of $\mathbb{N}$ where generally ordinality and cardinality do not coincide; they coincide only for $\mathbb{N}_1$ (whose physical counterpart is the BET model of AD-sorption, on the top of a layer directly adsorbed on the surface).

Interestingly, when applied for the description of evaporation, the case of AD-sorption on the top of a layer directly adsorbed on the surface, is the physical counterpart of integers, rather than natural numbers. Even more interesting is what happens in the case of condition (40). Indeed, for irreversible AD-sorption property 4 does not hold true, i.e. that it provides a model containing natural numbers when the Principle of Induction does not hold true.

Although much of mathematics can be built from natural numbers, the full body of mathematics requires a theory of sets. The common form of the theory of sets, ZF + AC, is based on the axioms of Extensionality, Foundation, Pairing, Union, Infinity and Power sets, and the axiom schemes of Separation and Replacement (defining the Zermelo–Fraenkel theory, ZF) plus the Axiom of Choice, AC. The construction of naturals in this theory is possible in different ways, of which the Von Neumann construction is the one most frequently employed.

Accepting other definitions of the basic number system (as the one proposed above) opens the problem of the most appropriate axioms accounting for them. If the number system does not satisfy the Principle of Induction, the underlying set theory should not involve the Axiom of Choice (because it implies Induction); instead, if the number system considered is formed by integers (rather than naturals) with contents, it seems plausible that Foundation should not be accepted as an axiom of the underlying set theory. This observation re-opens the problem of the degree of belief one may have in the axioms of set theory (Maddy 1988a,b).

CONCLUSIONS

This paper has been devoted to the construction of a rigorous kinetic theory of AD-sorption on reconstructible surfaces reducing to the Langmuir model in the limit where the degree of reconstruction is zero. The theory is essentially contained in reaction scheme (13) and refers

specifically to various cases through a suitable choice of the variable parameters. In the case of reversible AD-sorption onto a surface with a constant degree of reconstruction, the theory describes a system that relaxes exponentially to an equilibrium state coinciding with the equilibrium state of γ-ons. Reaction scheme (13) is useful for elucidating fundamental mathematical concepts such as the nature of natural numbers.

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APPENDIX: THE CASE OF LINEAR RECONSTRUCTION AND THE ELOVICH EQUATION

The cases of greater physical interest are those for which ε depends on N_o, essentially because this case captures a situation where the evolution of the exposed surface is controlled by its state rather than by its occupation. In this case, equations (15) and (16) become

$$\frac{dN_\bullet}{dt} = AN_o - BN_\bullet \tag{41}$$

$$\frac{dN_o}{dt} = \varepsilon(N_o)(AN_o - BN_\bullet) \tag{42}$$

Eliminating $AN_o - BN_\bullet$ between equations (41) and (42) leads to the relationship

$$dN_o = \varepsilon(N_o)dN_\bullet \tag{43}$$

which may be solved for $\varepsilon(N_o) \neq 0$ by the separation of variables:

$$\int_{N_o^0}^{N_o} \frac{dN_o}{\varepsilon(N_o)} = N_\bullet \tag{44}$$

(with N_o^0 being the amount of empty sites at $N_\bullet = 0$; N_o^0 must not be confused with the amount $N_o(0)$, i.e. the amount of empty sites at t = 0: $N_o^0 = N_o(0)$ only when $N_\bullet(0) = 0$). If $\varepsilon(N_o)$ does not change its sign during the integration interval, equation (44) can be solved for N_o, thus giving N_o as a function of $N_\bullet$:

$$N_o = \eta(N_\bullet) \tag{45}$$

Substituting $\eta(N_\bullet)$ for N_o in equation (41) gives

$$\frac{dN_\bullet}{dt} = A\eta(N_\bullet) - BN_\bullet \qquad (46)$$

which is the key equation of the theory. In fact, the equilibrium conditions are immediately obtained by putting $dN_\bullet/dt = 0$ in equation (46), i.e.

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

while the kinetics are determined through solving equation (46) employing the separation of variables:

$$\int_0^{N_\bullet(t)} \frac{dN_\bullet}{N_o^0\,\exp(bN_\bullet)} = At$$

$$\int_{N_\bullet(0)}^{N_\bullet(t)} \frac{dN_\bullet}{\eta(N_\bullet) - (B/A\,)N_\bullet} = At \qquad (47)$$

Just to provide an elementary (but important) application of this formula, we confine it to the case of adsorption on an initially clean surface (thus with $N_\bullet(0) = 0$) undergoing a reconstruction which varies linearly with the amount of available sites $(\varepsilon(N_o) = bN_o)$, from which desorption is neglible ($B = 0$). In this case, integrating equation (44) leads to $N_o = N_o^0\,\exp(bN_\bullet)$, whose insertion into equation (47) gives

$$\int_0^{N_\bullet(t)} \frac{dN_\bullet}{N_o^0\,\exp(bN_\bullet)} = At$$

Integration of this differential equation is straightforward:

$$N_\bullet(t) = -\frac{1}{|b|}\ln\!\left(1 - N_o^0 A|b|t\right) \qquad (48)$$

These kinetics have different behaviours according to the sign of b (Cerofolini 1995):

- for $b < 0$, it is convenient to make the sign explicit by putting $b = -|b|$ in equation (48), thus obtaining

$$N_\bullet(t) = \frac{1}{|b|}\ln\!\left(1 + N_o^0 A|b|t\right)$$

These kinetics predict a linear increase in $N_\bullet$ with t in the early stages

$$N_{\circ}^{0}A|b|t \ll 1 \Rightarrow N_{\bullet}(t) \simeq N_{\circ}^{0}At$$

eventually reducing to a logarithmic decrease for $N_{\circ}^{0}A|b|t \gg 1$. The occurrence of such a logarithmic time law is well known in adsorption (as well as oxidation) phenomena, where it is generally referred to as the Elovich equation.

- For $b > 0$, the kinetics are characterized by the same linear increase of $N_{\bullet}$ with t in the early stages but the reaction rate diverges at time $t = \left(N_{\circ}^{0}Ab\right)^{-1}$, thus providing a model for explosive reactions.

- For $b = 0$, equations (41) and (42) give $\forall t(N_{\circ} = N_{\circ}^{0})$ and $\forall t\left(N_{\bullet}(t) = N_{\circ}^{0}At\right)$, thus providing an example of kinetics depending linearly on time.