

## Fractional Statistical Theory of Adsorption of Polyatomics

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A new theoretical description of fractional statistical theory of adsorption (FSTA) phenomena is presented based on Haldane's statistics. Thermodynamic functions for adsorption of polyatomics are analytically developed. The entropy is characterized by an exclusion parameter  $g$ , which relates to the configuration of the admolecules and surface geometry. FSTA provides a simple framework to address a large class of complex adsorption systems. Comparisons of theoretical adsorption isotherms with experiments and simulations indicate that adsorption configuration and adsorption energy can accurately be assessed from this theory.

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The relevance of adsorption of polyatomics in interface and surface science is traced to its role as an elementary step in many practical and technological applications based on gas-solid interaction, as well as to the difficulties in describing analytically the thermodynamic functions of the adlayer when the nonspherical character of the adsorbate is accounted for. Although most adsorbates in nature are polyatomic, most of the rigorous analytical descriptions regarding statistical thermodynamics of adlayers rely upon the crude assumption of spherically symmetric admolecules [1–3]. Particularly, the lattice-gas approximation has provided a simple framework for analytical solutions based on the hypothesis of single-site occupation. Alternatively, analytical, phenomenological, and computer simulation approaches [4–10] have been helpful to understand the behavior of adsorbed  $n$ -alkanes, polymers, etc. Conceivably, the bottleneck in dealing with adsorption of large molecules is to properly calculate the entropic contribution to the thermodynamic potential arising from the spatial structure of the molecules; regardless, adsorption is assumed to take place either on a continuous or latticelike volume. Recent experimental contributions on equilibrium and kinetics of adsorbed  $n$ -alkanes on solid surfaces focus on the relevance of accounting for the structure and entropic effects of the adsorbed species [11,12].

Here, we present the basis of a fractional statistics thermodynamic theory of adsorption (FSTA) of polyatomics from a new conceptual framework inspired in the formalism of Haldane's statistics [13,14]. Thus, we obtain a remarkably simple approach to a complex problem as well as relate the parameters of the theory to physical properties of the system accessible from experiments. We put forward that adsorption of structured gases can be represented by a generalized statistics isomorphous to fractional statistics with an exclusion parameter  $g$  defined in the range  $g \geq 1$ . A simple description of polyatomic adsorption emerges from which the spatial configuration of the molecules in the adsorbed state, the topology of the adsorption lattice, and the adsorption heat can be ob-

tained through thermodynamic experiments. The advantages of FSTA for interpreting polyatomics adsorption data and characterization of the adsorption potential is shown by analyzing experimental adsorption isotherms of various adsorbates as well as simulation results in lattice gases.

In what follows, the basis of the proposed representation is introduced. One isolated molecule interacting with a regular solid surface confined in a fixed volume can be represented by an adsorption field having a total number  $G$  of local minima in the space of coordinates necessary to define the adsorption configuration (usually rendered by lattice sites in a discrete representation of the field). We rationalize  $G$  as being the number of equilibrium states available to a single molecule at infinitely low density. Depending on the ratio between the typical size of the molecule in the adsorbed configuration and the distance between neighboring minima, some states out of  $G$  are prevented from occupation upon adsorption of another molecule. Moreover, because of possible concurrent exclusion of states by two or more molecules, the number of states excluded per molecule,  $g(N)$ , being a measure of the "statistical" interactions, depends in general on the number of molecules  $N$  within the volume. Given  $(N - 1)$  identical molecules confined in a container of fixed volume  $V$ , the number of states available for addition of the  $N^{\text{th}}$  molecule is  $d_N = G - \sum_{N'=1}^{N-1} g(N') = G - G_0(N)$  [13]. Accordingly, we propose to describe the general class of physical systems addressed here by means of a generalized statistics with  $g(N) \geq 1$  for which the number of configurations of a system of  $N$  molecules and  $G$  states is  $W(N) = (d_N + N - 1)!/[N!(d_N - 1)!]$  [13].

By assuming  $U_0$  being the adsorption energy per particle, the Helmholtz free energy  $F(N, T, V)$  and the partition function  $Q(N, T, V) = W(N) \exp(-\beta N U_0) q_i^N$  relate through  $\beta F = -\ln Q$ , where  $\beta = 1/k_B T$  and  $q_i$  is the partition function from the internal degrees of freedom of a single molecule in the adsorbed state. Thus, a general form for the chemical potential of noninteracting adsorbed polyatomics is obtained from  $\mu = (\frac{\partial F}{\partial N})_{T,V}$  as:

$$\beta\mu = \ln \left[ \frac{n[1 - \tilde{G}_0(n) + n]^{\tilde{G}'_0(n)}}{[1 - \tilde{G}_0(n)]^{\tilde{G}'_0(n)}} \right] - \ln K(T), \quad (1)$$

where  $n = N/G$  is the density ( $n$  finite as  $N, G \rightarrow \infty$ ), which is proportional to the standard surface coverage  $\theta$ ,  $n = a\theta$ ,  $\theta$  being either the ratio  $N/N_m$  or the ratio  $v/v_m$ , where  $N$  ( $v$ ) is the number of admolecules (adsorbed amount) at given  $\mu, T$ , and  $N_m$  ( $v_m$ ) is the one corresponding to monolayer completion. In addition,  $\tilde{G}_0(n) \equiv \lim_{N, G \rightarrow \infty} G_0(N)/G$ ,  $\tilde{G}'_0 \equiv d\tilde{G}_0/dn$ , and  $K(T) = q_i \exp(-\beta U_0)$ . Hereafter we examine the simplest approximation within FSTA, namely  $g = \text{const}$ , which is rather robust as it will be shown below. Considering that  $\tilde{G}_0 = gn$  and  $\tilde{G}'_0 = g$ , a particular isotherm function arises from Eq. (1)

$$K(T) \exp[\beta\mu] = \frac{a\theta[1 - a\theta(g-1)]^{g-1}}{[1 - a\theta g]^g}. \quad (2)$$

It can be demonstrated that Eq. (2) reduces to the rigorous isotherm of noninteracting chains ( $k$ -mers) adsorbed flat on a one-dimensional lattice [9] if  $g$  equals the number of chain units (size)  $k$ . This is already a simple example of the underlying relationship between the statistical exclusion parameter  $g$  and the spatial configuration of the admolecule.

We shortly mention some examples out of a whole variety of adsorption configurations that the proposed formalism allows to deal with. Let us consider adparticles composed by  $k$  elementary units in which  $k'$  out of  $k$  units of the molecule are attached to surface sites and  $(k - k')$  units are detached and tilted away from them. For a lattice of  $M$  sites,  $\theta = k'N/M$ . Thus, for a molecule with  $k$  units, each of which occupying an adsorption site,  $k' = k$  and  $G = Mm$ , where  $m$  is the number of distinguishable configurations of the molecule per lattice site (at zero density) and depends on the lattice/molecule geometry. Then  $1/a = k'm$ . For instance, straight  $k$ -mers adsorbed flat on sites of a square lattice would correspond to  $m = 2$ ,  $g = 2k$ , and  $a = 1/(2k)$ . On the other hand,  $m = 1$ ,  $g = 1$ , and  $a = 1$  represent the case of end-on (normal to the surface) adsorption of  $k$ -mers. Instead,  $m = 1$ ,  $g = k'$ , and  $a = 1/k'$  represent an adsorption configuration in which  $k'$  units of the  $k$ -mer are attached to a one-dimensional lattice and  $(k - k')$  units at the ends are detached.

It is worth to note that in general, adsorbed molecules may adopt different configurations as the density increases. In this case, the values obtained for  $g$  from experiments will depend on the pressure range analyzed, according to the general form of Eq. (1). In turn,  $a$  relates to the low density limit  $\theta \rightarrow 0$ ,  $\beta\mu \approx \ln a\theta - \ln K(T)$ .

Although no interactions between admolecules have been considered in the derivation in order to obtain an explicit analytical isotherm function, the fact that ad-ad interaction may be appreciable can be accounted through a mean-field contribution by substituting in Eq. (1)  $\beta\mu \rightarrow$

$\beta\mu - \beta w\theta$ , being  $w$  the lateral interaction per molecule at monolayer completion.

Analysis of simulated and experimental results have been carried out in order to evince the physical significance of  $g$  and  $a$  in terms of spatial configuration of the adsorbed molecule/surface geometry. Thus, experimental adsorption isotherms of oxygen [15,16] and propane [17] in 5A and 13X zeolites, respectively, were examined in terms of the new isotherm function. In our analysis, Eq. (2) was used assuming that: (i) since  $g = \text{const}$ , if one molecule has  $m$  distinguishable ways of adsorbing per lattice site at zero density, then  $g = mk'$  [ $a = 1/(mk')$ ] states are excluded when one  $k$ -mer is adsorbed occupying  $k'$  sites on the lattice; (ii) ad-ad interaction energy is introduced through a mean-field term as stated before. In addition, given that the analyzed experimental isotherms were reported in adsorbed amount  $v$  against pressure  $p$ , we rewrite Eq. (2) in the more convenient form:

$$K(T)p/p_o = \frac{(v/v_m)[g - (g-1)v/v_m]^{g-1}}{[g - g(v/v_m)]^g} \times \exp[\beta w(v/v_m)], \quad (3)$$

where  $\exp[\beta w(v/v_m)]$  is the mean-field term,  $p = p_o \exp(\beta\mu)$  and  $K(T) = K_\infty \exp(-\beta H_{st})$  is the equilibrium constant,  $H_{st}$  being the isosteric heat of adsorption.

Adsorption isotherms of  $O_2/5A$  are shown in Fig. 1. Symbols are experimental data and lines represent theoretical results from Eq. (3). Experimental data were taken from two different sources in the literature, from Miller *et al.* [15] and Danner *et al.* [16]. In the first set of data (empty symbols) [15], the amount adsorbed was measured in units of the number of molecules per cavity. In the other case (full symbols) [16], the amount adsorbed was re-

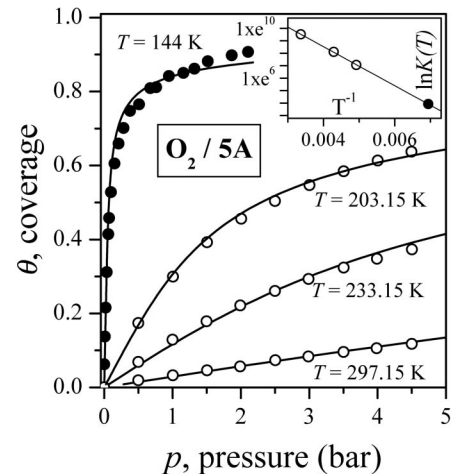


FIG. 1. Adsorption isotherms for  $O_2/5A$  fitted by FSTA. Empty and full symbols correspond to data from Refs. [15,16], respectively. Lines correspond to Eq. (3). Inset:  $K(T)$  arising from fitting.  $H_{st}^{FSTA}$  reported in Table I is the absolute value of the slope of the solid line.

TABLE I. Table of fitting parameters of data in Figs. 1 and 2.  $H_{st}^{FSTA}$ ,  $H_{st}^{exp}$ ,  $w^{FSTA}$  and  $w^{exp}$  are given in kcal/mol (absolute values).  $D$  is defined as the ratio between the absolute value of the difference between the experimental and the corresponding theoretical value, averaged over the total set of data.

System	k	m	g	$\nu_m$	$H_{st}^{FSTA}$	$H_{st}^{exp}$	$w^{FSTA}$	$w^{exp}$	$D$
O <sub>2</sub> /5A	2	2	4	12 <sup>a</sup> -130.9 <sup>b</sup>	3.10	3.37 <sup>c</sup>	0.72	0.54 <sup>d</sup>	5.60%
C <sub>3</sub> H <sub>8</sub> /13X	3	1	3	5.75	6.94	6.81 <sup>e</sup>	1.27	0.50 <sup>f</sup>	2.08%

<sup>a</sup>  $\nu_m$  is expressed in molecules/cavity [15].

<sup>b</sup>  $\nu_m$  is expressed in  $cc_{STP}/g$  of adsorbent [16].

<sup>c</sup> Represents experimental values from Ref. [15].

<sup>d</sup> Represents experimental values from Ref. [17].

<sup>e</sup> Simulation data from Ref. [18].

<sup>f</sup> C<sub>3</sub>H<sub>8</sub> - C<sub>3</sub>H<sub>8</sub> interaction energy in the liquid phase [17].

ported in units of  $cc_{STP}$  per gram of adsorbent. In order to homogenize the plots, we have represented the amount adsorbed by using the adimensional surface coverage  $\theta = \nu/\nu_m$ .

The fit was carried out in two steps: (i) based on previous numerical simulations [18], we fix  $g = 4$  ( $k' = k = 2$  and  $m = 2$ ). Then, we determine, by multiple fitting, the set of parameters  $[K(T), \nu_m, w]$  leading to the best fit to the experimental data of O<sub>2</sub>/5A from Ref. [15] in the whole pressure and temperature range. The fitting parameters are indicated in Table I. The values obtained for  $H_{st}$ , from the plot  $\ln K(T)$  vs  $1/T$ , and  $w$  are in excellent agreement with the experimental value of  $H_{st}$  reported in Ref. [19] and the simulation calculation of  $w$  in Ref. [18]. With respect to  $\nu_m$ , it was not possible from the work of Razmus *et al.* [19] to estimate  $\nu_m$  in order to compare with the one from Eq. (3). However,  $\nu_m$  was independently validated through a second stage of fitting; (ii) the values of  $g$ ,  $K(T)$ , and  $w$  arising from (i) were fixed. Then,  $\nu_m$ , set as to fit the experimental isotherm measured by Danner *et al.* [16], agrees with the monolayer volume reported in Ref. [16]. Based in the consistency of this analysis, O<sub>2</sub> appears to adsorb flat with two possible orientations on a two-dimensional layer defined by the cavity's inner surface.

Figure 2 shows adsorption isotherms of C<sub>3</sub>H<sub>8</sub> in a 13X zeolite. Lines correspond to FSTA and symbols represent experimental data from [17]. As widely accepted, an alkane chain is considered a "bead segment" in which each methyl group is represented as a single site (bead). In this frame, we fix  $k = 3$  for propane. In addition, the length of propane (6.7 Å) is relatively large with respect to the diameter of the cavity (11.6 Å). This fact suggests that the molecules should adsorb aligned along a preferential direction. Otherwise, 5-6 molecules would hardly fit in the cavity. Accordingly, we fix  $g = 3$  ( $k' = k = 3$  and  $m = 1$  as in the one-dimensional case). Under these considerations, analytical isotherms in Fig. 2 were obtained by multiple fitting the set of parameters  $K(T)$ ,  $\nu_m$ , and  $w$  as in Fig. 1.

As shown in Fig. 1,  $H_{st}$ , obtained from the slope of  $\ln K(T)$  vs  $1/T$ , is in very good agreement with experi-

mental data from Ref. [17]. As in the experiment, the resulting value of  $\nu_m$  is smaller than 6 molecules per cavity, and the fractional value of  $\nu_m$  ( $= 5.75$ ) is indicative that some molecules may stand across the cavity's windows. Concerning the lateral interaction at full coverage, the ratio between the value of  $w$  from fitting and the molecular interaction C<sub>3</sub>H<sub>8</sub> - C<sub>3</sub>H<sub>8</sub> in the liquid phase,  $\epsilon$ , reported in Ref. [17] is  $w/\epsilon \approx 2.5$ . This value indicates that each propane molecule in the adsorbed phase at maximum loading interacts, in average, with 2.5 neighbors, and reinforces the argument that the system can be treated as a quasi-one-dimensional system.

The deviations between experimental and fitting curves in Figs. 1 and 2 were 5.60% and 2.08%, respectively (Table I). These values are lower than the typical errors in measurements of adsorption, which reinforces the robustness of the fits in the present work. In addition, it is worth emphasizing that a rather artificial model with eight fitting parameters was necessary to interpret analogous data in Ref. [17]. In the present description, the complexity of the entropy of polyatomics is characterized by the single parameter  $g$  carrying meaningful quantitative information about the spatial configuration of the admolecule.

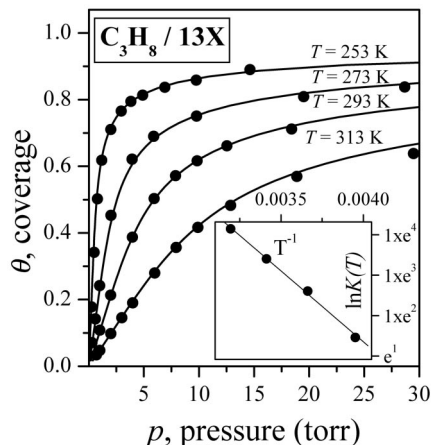


FIG. 2. Idem to Fig. 1 for C<sub>3</sub>H<sub>8</sub>/13X. Circles correspond to data from Ref. [17].

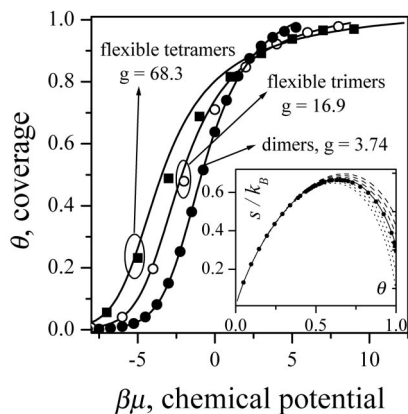


FIG. 3. Comparison between Monte Carlo simulations of dimers, trimers, and tetramers adsorbed on square lattices and theoretical isotherm from FSTA Eq. (3).  $g$  values from best fitting are indicated in the figure. Inset: configurational entropy versus coverage for dimers on square lattices. Symbols represent simulation data and lines provide theoretical results for different values of  $g$  as indicated in the text.

In order to illustrate the applicability and versatility of FSTA to describe systems more complex than the one in the experiments analyzed here, we show in Fig. 3 the fit (solid lines) to numerical isotherms (symbols) of dimers, flexible trimers, and flexible tetramers [20] adsorbed flat on a square lattice. Solid lines represent the best fitting to computer experiments in the crudest approximation [ $g = \text{const}$ , Eq. (2)] to the general isotherm of Eq. (1). The values obtained for  $g$  in all cases are very consistent to the ideal value  $g = mk$ . It is worth mentioning that, at this elementary degree of approximation, FSTA is already more accurate than the classical Flory's theory [4] of adsorbed chains as well as the multisite-adsorption approaches of Refs. [7,9].

For the case of dimers, the inset in Fig. 3 shows a comparison between the configurational entropy per site,  $s$ , versus coverage from simulation and the corresponding ones obtained from FSTA [being  $S = -(\frac{\partial F}{\partial T})_{N,M}$  and  $s \equiv S/M$ ] for different values of  $g$ . As it was calculated for the isotherm, the best fit corresponds to  $g = 3.74$  (solid line). The three curves in dashed (dotted) lines correspond to increments (decrements) of 2%, 4%, and 6% with respect to  $g = 3.74$ . As it can be clearly visualized, small variations of  $g$  provide notable differences in the entropy curves. Thus, the statistical exclusion parameter  $g$  results highly sensitive to the adparticle's spatial configuration. The more compact the configuration of the segments attached to the surface sites, the smaller  $g$ . For instance,  $g$  may vary from  $g = 6$  ( $g = 8$ ) for straight trimers (tetramers), to  $g = 18$  ( $g = 72$ ) for flexible trimers (tetramers).

In conclusion, the basis of an original description (FSTA) of polyatomic adsorption phenomena based

upon the foundations of Haldane's statistics have been presented and the fundamental thermodynamic functions developed. It comprises a small set of parameters having a precise physical meaning that can be obtained from thermodynamic experiments. Particularly, the concept of statistical exclusion ( $g \geq 1$ ) allows to handle the complexity of the entropy of adsorbed polyatomics traced to the adsorbate's configuration and interactions, and thus, the spatial mode of adsorption can be quantitatively assessed from experiments through the parameter  $g$ . Additionally, Eq. (1) provides the basis to investigate the changes of adsorbate's configuration upon density [configurational spectroscopy,  $G'(N)$ ] from thermodynamic data. FSTA gives a framework and compact equations to consistently interpret thermodynamic adsorption experiments ranging from simple species to elaborated polyatomics such as alkanes, alkenes, and other hydrocarbons on regular surfaces.

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