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Generalized statistical description of adsorption of polyatomics

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Abstract

Multisite-occupancy adsorption is described as a fractional statistic problem, based on Haldane's statistics. Site exclusion is characterized by a statistical exclusion parameter, g, which relates to the molecular size and lattice geometry. A general adsorption isotherm is obtained and comparisons with experiments indicate that the spatial configuration of adsorbed molecules and lateral interactions may accurately be assessed from this theory. In addition, the theoretical framework developed in this paper allows to describe orientational transitions occurring in adlayers of polyatomics.
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1. Introduction

Theoretical descriptions of adsorption of polyatomics are constrained by the structure of the adsorbate, making it very difficult to obtain the thermodynamic functions of the adlayer when the non-spherical character of the adsorbate is accounted for. Although most adsorbates are polyatomic, most of the rigorous or approximate analytical models regarding statistical thermodynamics of adlayers rely upon the crude assumption of spherically symmetric admolecules [1–3]. Naturally, the bottleneck in dealing with adsorption of polyatomics is to properly calculate the entropic contribution to the thermodynamic potential of the non-spherical character, regardless the adsorption is assumed to take place either on a continuum or lattice-like substrate. Particularly, the lattice gas approximation has provided a simple framework for analytical developments based on the hypothesis of single-site occupation. This reduction to simplicity has not only been of academic interest but essential for interpretation of adsorption experiments, determination of gas–solid interaction potentials, and characterization of solid adsorbents.

The fact that the calculation of configurational entropy of a lattice gas with multiple site occupation seems a hopeless task within the formalism of standard statistical mechanics has hindered the

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development of simple approaches for adsorption of polyatomics qualitatively better than the early seminar contributions of Flory–Huggins on polymer adsorption [4,5]. Moreover, recent contributions have shown that it makes much sense to accurately estimate the configurational entropy of the adlayer when the molecules occupy more than two adsorption sites [4,6–14]. From this consideration it results for instance that the rigorous isotherm for non-interacting linear species in $1D$ is, in the lattice gas approximation $k\exp\beta\mu = \theta[1-((k-1)/k)\theta]^{k-1}/(1-\theta)^k$ [10] instead of $k\exp\beta\mu = \theta/(1-\theta)^k$ [4,5] predicted by the Flory–Huggins approximation. Thus, the consideration of multiple occupation of sites in multilayer adsorption [15] leads to rather significant effects on the adsorption isotherms, and consequently on the surface and adsorption heat obtained from experiments, compared with the well-known BET model [16].

In this contribution, we present the basis of a fractional statistics thermodynamic theory of adsorption (FSTA) of polyatomics from a new standpoint based on the formalism of Haldane's statistics [17,18]. The appealing feature of Haldane's statistics or quantum fractional statistics (QFS) is that a system of interacting particles confined in a finite region of the space can be characterized by an "statistical exclusion parameter", g, accounting for the number of states that are excluded from the states spectrum when a particle is added to the system. The relevant range of g in quantum physics is $0 \le g \le 1$ being the limiting cases of bosons and fermions statistics, respectively. Although QFS has been interpreted in the context of quantum systems as to describe one-dimensional quantum fluids, fractional quantum Hall effect, quantum thermal conductance, etc., we shown here that adsorption of structured lattice gases can be treated in the framework of a generalized statistics with a exclusion parameter defined in the range $g \ge 1$. In addition, the advantages of using this simple description as a tool for interpreting polyatomics adsorption data and characterization of the adsorption potential is shown by analyzing simulation results in lattice and off-lattice gases as well as experimental adsorption isotherm of various adsorbates.

The paper is organized as follows: the basis of FSTA are presented in Section 2. In Section 3, experimental data for oxygen adsorbed in 5A zeolite and propane adsorbed in 13X zeolite are analyzed by using FSTA. Finally, general conclusions are given in Section 4.

2. Theory

The formalism of QFS have been recently developed on the basis of a generalization of the Pauli's exclusion principle proposed by Haldane [17,18]. Haldane's statistics relies on the fact that, given $(N-1)$ identical particles confined in fixed volume, each of which having G accessible states at infinitely low density, the number of states available to a Nth particle added to the volume is

$$d_N = G - \sum_{N'=1}^{N-1} g(N') = G - G_0(N), \tag{1}$$

being the number of states excluded per particle, $g(N)$, a measure of the statistical interactions. In addition, the number of configurations for a system of N particles and G states is:

$$W(N) = \frac{(d_N + N - 1)!}{[N!(d_N - 1)!]} = \frac{[G - G_0(N) + N - 1]!}{\{N![G - G_0(N) - 1]!\}}. \tag{2}$$

Clearly, $g(N) = 0\,[G_0(N) = 0]$ and $g(N) = 1\,[G_0(N) = N-1]$ holds for bosons and fermions, respectively.

Here, we propose to extend this statistics as to describe classical systems like the adsorption of polyatomic molecules at the gas–solid interface. The arguments follow [19]: 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, $g(N)$, depends in general on the number of molecules N within the volume. Accordingly, given $(N-1)$ identical molecules adsorbed on a surface of M sites, the number of states available to a Nth one added to it can be obtained from Eq. (1) with $g(N) \geq 1$.

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 non-interacting adsorbed polyatomics is obtained from $\mu = (\partial F/\partial N)_{T,V}$ as:

$$\beta\mu = \ln\left[\frac{n[1-\tilde{G}_0(n)+n]^{(\tilde{G}_0'-1)}}{[1-\tilde{G}_0(n)]^{\tilde{G}_0'}}\right] - \ln K(T) \qquad (3)$$

where $n = N/G$ is the density (n finite as $N, G \to \infty$), which is proportional to the standard surface coverage θ, $n = a\theta$, θ 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 μ, T and N_m (v_m) is the one corresponding to monolayer completion. In addition, $\tilde{G}_0(n) \equiv \lim_{N,G\to\infty} G_0(N)/G$, $\tilde{G}_0' \equiv \mathrm{d}\tilde{G}_0/\mathrm{d}n$ and $K(T) = q_i \exp(-\beta U_0)$. Hereafter, we examine the simplest approximation within FSTA, namely g =constant, 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. (3)

$$K(T)\exp[\beta\mu] = \frac{a\theta[1-a\theta(g-1)]^{g-1}}{[1-a\theta g]^g}. \qquad (4)$$

It can be demonstrated that Eq. (4) reduces to the rigorous isotherm of non-interacting chains (k-mers) adsorbed flat on a one-dimensional lattice [10] if g equals the number of chain units (size) k. This is already a simple example of the underlaying 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 $a = 1$ represents the case of end-on (normal to the surface) adsorption of k-mers. Instead, $m = 1$, $g = k'$ and $a = 1/k'$ represents 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. (3). In turns, a relates to the low density limit $\theta \to 0$, $\beta\mu \approx \ln a\theta - \ln K(T)$.

Although, no detailed 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. (3) $\beta\mu \to \beta\mu - \beta w\theta$, being w the lateral interaction per molecule at monolayer completion.

3. Comparison with simulated and experimental results

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 propane [20] and oxygen [21,22] in 5A and 13X zeolites, respectively, were examined in terms of the new isotherm function. In our analysis, Eq. (4) was used assuming that: (i) since g =constant, 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. (4) in the more convenient form:

$$K(T)\,\frac{p}{p_0} = \frac{(v/v_m)[g-(g-1)v/v_m]^{g-1}}{[g-g(v/v_m)]^{g}} \times \exp\left[\beta w(v/v_m)\right] \tag{5}$$

where $\exp[\beta w(v/v_m)]$ is the mean-field term, $p = p_0 \exp(\beta\mu)$ and $K(T) = K_\infty \exp(-\beta H_{st})$ is the equilibrium constant, H_{st} being the isosteric heat of adsorption.

Fig. 1 shows adsorption isotherms of C_3H_8 in a 13X zeolite. Lines correspond to FSTA and symbols represent experimental data from [20]. 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). Then, we determine, by multiple fitting, the set of parameters $[K(T), v_m, w]$ leading to the best fit to the experimental data of C_3H_8/13X from Ref. [20] in the whole pressure and temperature range.

The fitting process is as follows. We considered the least-squares statistics [23]. Thus, suppose that

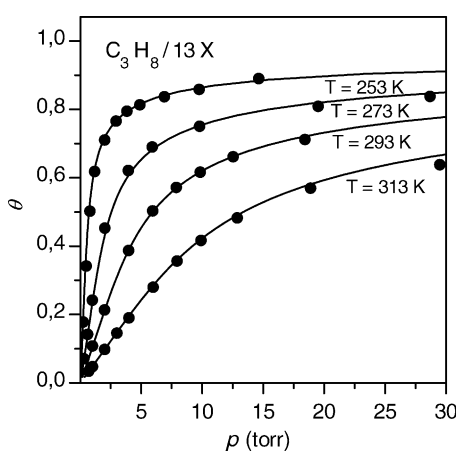

Fig. 1. Adsorption isotherms for C_3H_8 adsorbed in 13X zeolite fitted by FSTA. Symbols correspond to data from Ref. [20] and lines represent theoretical results from Eq. (5).

we are fitting n_m data points (x_i, y_i, z_i), $i = 1, \ldots, n_m$, to a model that has L adjustable parameters a_j, $j = 1, \ldots, L$. The model predicts a functional relationship between the measured independent and dependent variables,

$$z(x, y) \equiv z(x, y; a_1 \ldots a_L) \tag{6}$$

where the dependence on the parameters is indicated explicitly on the right-hand side. What, exactly, do we want to minimize to get fitted values for the a_j's? The first thing that comes to mind is the familiar least-squares fit, minimize over $a_1 \ldots a_L$:

$$\sum_{i=1}^{n_m} [z_i - z(x_i, y_i; a_1 \ldots a_L)]^2 \tag{7}$$

The parameters of the model are then adjusted to achieve a minimum in function (7), yielding best-fit parameters. The adjustment process is thus a problem in minimization in many dimensions.

In our particular case, the least-squares estimation of the isotherm parameters was performed for each adsorbate by minimizing the sum of the square difference between the experimental pressure and the predicted pressure, over all n_m data points corresponding to the complete set of isotherms. That is, the function $p(v, T) \equiv p(v, T; v_m, K(T), w)$ (from Eq. (5)) corresponds to $z(x, y) \equiv z(x, y; a_1 \ldots a_L)$, being (v, T) and $(v_m, K(T), w)$ dependent variables and adjustable parameters, respectively. In the case of Fig. 1, the fitting parameters are indicated in Table 1.

As in the experiment, the resulting value of v_m is smaller than six molecules per cavity, and the fractional value of $v_m (= 5.75)$ 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_3H_8–C_3H_8 in the liquid phase, ε, reported in Ref. [20] is $w/\varepsilon \approx 2.5$. 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.

An excellent agreement was also obtained in Fig. 2, by fitting non monotonically increasing data (in Fig. 2, we carried out the fitting of the derivative of the adsorbed amount versus pressure and obtained a good agreement).

Table 1
Table of fitting parameters of data in Figs. 1 and 3

System	k	m	g	v_m	H_{st}^{FSTA}	H_{st}^{exp}	w^{FSTA}	w^{exp}	D (%)
O_2/5A	2	2	4	12 (a)–130.9 (b)	3.10	3.37 (c)	0.72	0.54 (e)	5.60
C_3H_8/13X	3	1	3	5.75	6.94	6.81 (d)	1.27	0.50 (f)	2.08

H_{st}^{FSTA}, H_{st}^{exp}, w^{FSTA} and w^{exp} are expressed in kcal/mol (absolute values given). v_m is expressed in molecules/cavity (a) and cc_{STP}/g of adsorbent (b) for data from Refs. [21] and [22], respectively. (c) And (d) represent experimental values from Refs. [21] and [20], respectively; (e), simulation data from Ref. [24] and (f), C_3H_8–C_3H_8 interaction energy in the liquid phase [20].

The differences between experimental and theoretical data can be very easily rationalized with the help of the deviation D, which 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:

$$D = \sum_{i=1}^{n_m} \left\{ 100 \left| \frac{v_{\text{theo}}^i - v_{\text{sim}}^i}{v_{\text{sim}}^i} \right| \right\}. \quad (8)$$

The deviation between the set of experimental data and the fitting curves in Fig. 1 was 2.08% (see Table 1). This value is lower than the typical experimental errors in measurements of adsorption, which reinforces the robustness of the fits in the present contribution. In addition, it is worth emphasizing that a rather artificial model with eight fitting parameters was necessary to interpret analogous data in Ref. [20]. In the present description of adsorption, the complexity of the entropy of adsorbed polyatomics is characterized by the single parameter g carrying meaningful quantitative information about the spatial configuration of the admolecule.

Adsorption isotherms of O_2/5A are shown in Fig. 3. Symbols are experimental data and lines represent theoretical results from Eq. (5). Experimental data were taken from two different sources in the literature, from Miller et al. [21] and Danner and Wenzel [22]. In the first set of data (empty symbols) [21], the amount adsorbed was measured in units of the number of molecules per cavity. In the other case (full symbols) [22], the amount adsorbed was reported 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 $\theta = v/v_m$.

The fit was carried out in two steps: (i) based on previous numerical simulations [24], we fix $g = 4$ ($k' = k = 2$ and $m = 2$). Under these considerations, analytical isotherms in Fig. 3 were obtained by multiple fitting the set of parameters $K(T)$, v_m and w as

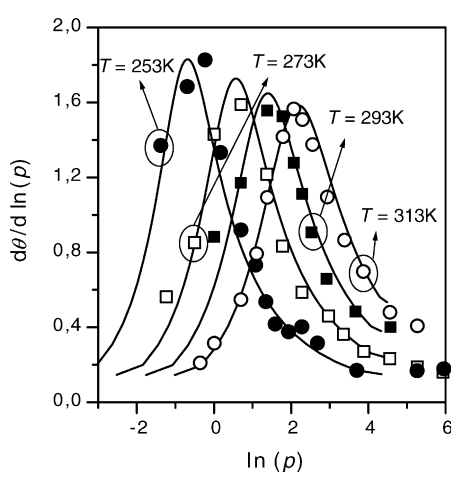

Fig. 2. Derivative of the adsorbed amount vs. pressure (ln p) for the same set of data plotted in Fig. 1.

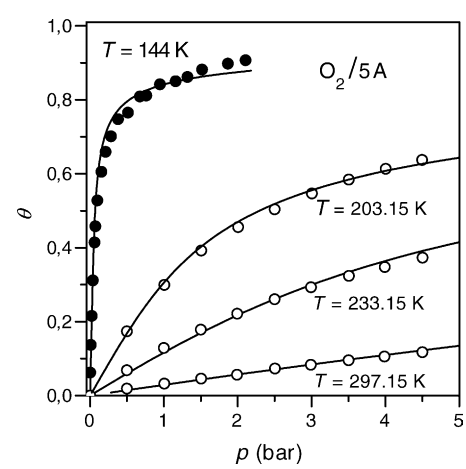

Fig. 3. Adsorption isotherms for O_2 adsorbed in 5A zeolite. Empty and full symbols correspond to data from Refs. [21] and [22], respectively. Lines correspond to the adsorption isotherm function of Eq. (5).

in Fig. 1. The value obtained for w is in excellent agreement with the simulational calculation of w in Ref. [24]. With respect to v_m, it was not possible from the work of Razmus and Hall [25] to estimate v_m in order to compare with the one from Eq. (5). However, v_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, v_m, set as to fit the experimental isotherm measured by Danner and Wenzel [22], agrees with the monolayer volume reported in Ref. [22]. The deviation between experimental and fitting curves was 5.60% (see Table 1). Based in the consistency of this analysis, O_2 appears to adsorb flat with two possible orientations on a two-dimensional layer defined by the cavity's inner surface.

The values for H_{st} in Figs. 1 and 3 were obtained from the slope of $\ln K(T)$ versus $1/T$. This procedure is shown in Fig. 4. The fitting results, which are presented in Table 1, are in excellent agreement with the experimental value of H_{st} reported in Ref. [20] (C_3H_8/13X) and Ref. [25] (O_2/5A).

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. 5 the fit (solid lines) to numerical isotherms (symbols) of dimers, flexible trimers and flexible tetramers adsorbed flat on a square lattice [a flexible k-mer is a chain of monomers occupying k adjacent sites of the lattice (without overlapping)]. Solid lines represent the best fitting to computer experiments in the crudest approximation [$g =$ constant, Eq. (4)] to the general isotherm of Eq. (3). 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. [8,10].

For the case of dimers, Fig. 6 shows a comparison between the configurational entropy per site, s, versus

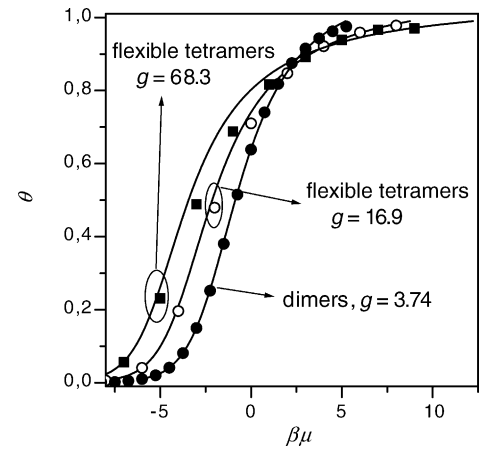

Fig. 5. Comparison between Monte Carlo simulations of dimers, trimers and tetramers adsorbed on square lattices and theoretical isotherm from FSTA [Eq. (4)]. g values from best fitting are indicated in the figure for each case.

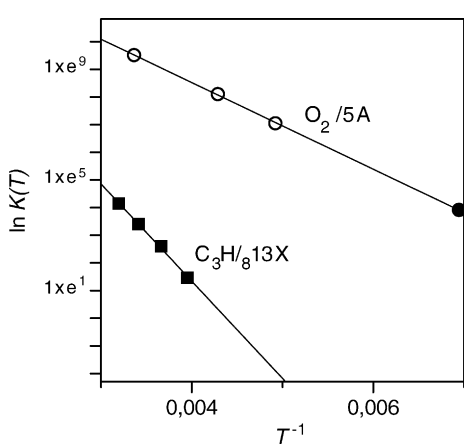

Fig. 4. Temperature dependence of equilibrium constant, $K(T)$, arising from fitting. Squares, empty circles and full circles correspond to fitting from Refs. [21], [22] and [20], respectively. H_{st}^{FSTA} reported in Table 1 is the absolute value of the slope of the solid line.

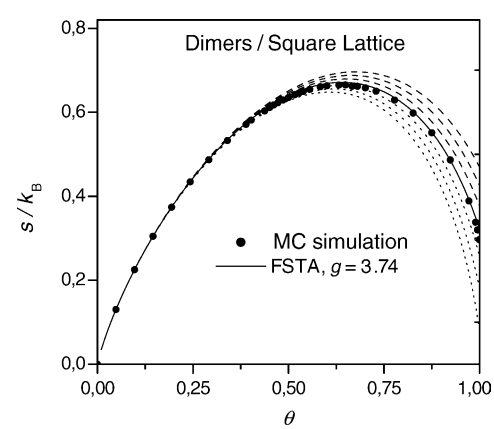

Fig. 6. Configurational entropy versus coverage for dimers adsorbed on square lattices. Symbols represent simulation data and lines provide theoretical results for different values of g as indicated in the text.

coverage from simulation [11] and the corresponding ones obtained from FSTA [being $S = -(\partial F/\partial T)_{N,M}$ 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. 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). From the previous considerations, it arises that the best fitting of adsorption data within the framework of the FSTA shows a high sensitivity to the value of g for the cases studied. This represents an evidence of the physical and experimental significance of g.

4. Conclusions

The basis of an original theory (FSTA) of polyatomic adsorption phenomena based upon the foundations of Haldane's statistics have been presented and experimental data of C_3H_8/13X [20] and O_2/5A [21,22] have been analyzed by using FSTA model. The superiority of this description relies in its scope (potentially applicable to a wide set of adsorption systems ranging from small polyatomics, hydrocarbons, and perhaps up to light polymers), its simplicity (closed forms of functions), the smallest number of parameters necessary to account for the surface–molecule/molecule–molecule interactions and the configuration state of the admolecule, and the proposition of a general relationship [Eq. (3)] to address the configuration spectrum of the admolecules upon density [i.e. $\tilde{G}_0'(N)$] from thermodynamic (adsorption) data. A more comprehensive analysis of simulated and experimental systems, necessary to determine the extent of the model to interpret real systems is in progress.

Acknowledgments

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