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Fractional statistical analysis of adsorption

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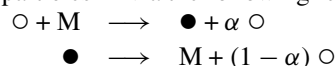
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Abstract

If a system described in terms of empty and filled states (\circ and \bullet , respectively) interacts with particles M via the following reactions:



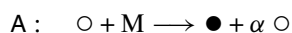
(with α being a real number), then it may be described in terms of fractional statistics. On the other hand, provided that the states are identified with adsorption sites, this scheme may be used, according to the value assigned to α , for the description of adsorption–desorption phenomena such as the inhibition of empty sites by the adsorption of polyatomic molecules, multilayer adsorption, and the branched growth of dendrimers. Not only does the fractional statistical treatment reproduce the well-known Langmuir and Brunauer–Emmett–Teller isotherms for $\alpha = 0$ and $\alpha = 1$, but also it provides the adsorption isotherms for all other values of α . It is also shown that considered as a function of the parameter α the equilibrium isotherm undergoes a catastrophe at $\alpha = 1$.

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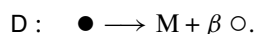
1. Introduction

The concept of anyons (particles with fractional statistics) has been proved, in past years, of great usefulness in the description of several phenomena in condensed matter [1].

Denoting with \circ and \bullet empty and filled states, respectively, the occupation of an empty state by a particle M with the simultaneous formation of α new empty states may be described by the following discrete process:



and similarly the loss of the particle from a filled state with the formation of β empty states:



Denoting with $\prod_{J=1}^N P_J$ a sequence of events $P_1 \cdot P_2 \cdots P_N$ with $\forall J (P_J \in \{A, D\})$, the necessary condition in order a system undergoing processes A and D admits equilibrium states is that the sequences $A \cdot D$ and $D \cdot A$ are reversible cycles, which implies $\beta = 1 - \alpha$. In this case one may consider the equilibrium



and study which isotherms it sustains.

Following Haldane [1], together with the number $N_o(0)$ of the original empty sites in the given volume V , one has to consider the number $N_o(N)$ of sites available for the adsorption of the N th particle when $N - 1$ particles have already been adsorbed:

$$\begin{aligned} N_o &= N_o(0) - \sum_{J=1}^{N-1} (1 - \alpha_J) \\ &=: N_o(0) - \bar{N}_o, \end{aligned}$$

where α_J is the value of α in process A corresponding to the J th filling of an empty state. For state-counting purposes at fixed particle numbers, the particles may be regarded as bosons in a Fock space of dimension N_o as well as fermions in a Fock space of dimension $N_o + N - 1$, regardless of the true—boson or fermion—nature of the particles (the particles are true bosons (or fermions) when N_o (or $N_o + N - 1$) remains constant with N). Conversely, any situation which can be described by equilibrium (1) runs in the above situation quite irrespective of the particle statistics. According to the analysis of Murthy and Shankar [2], the parameter governing fractional statistics is manifested even at high temperature in thermodynamic quantities like the second virial coefficient. Since classical particles are nothing but quantum particles whose statistics is mute in the considered temperature regime, the above considerations can be applied in all situations described by equilibrium (1).

Following Wu [3] and Isakov [4], a statistical description of this system is achieved considering the number of configurations $W(N)$ of N particles and N_o states:

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

Assuming that the particles are independent of one another and are stabilized by an energy ϵ , the partition function $Z(N, T)$ is given by

$$Z(N) = W(N) \exp(-\epsilon N / k_B T) z^N,$$

where k_B is the Boltzmann constant and z is the single-particle partition function associated with the internal degrees of freedom of the particle in the stabilizing field. The Helmholtz free energy F and chemical potential μ are then calculated by the well-known relationships

$$F = -k_B T \ln Z, \quad \mu = \partial F / \partial N.$$

In the thermodynamic limit ($N, N_o(0) \rightarrow +\infty$, $N/N_o(0) = n$ finite) the chemical potential is given by

$$\frac{\mu}{k_B T} = \ln \left(\frac{n(n - (\bar{v} - 1))^{\bar{v}' - 1}}{(1 - \bar{v})^{\bar{v}'}} \right) - \ln K, \quad (2)$$

where \bar{v} is the thermodynamic limit of $\bar{N}_o/N_o(0)$, $\bar{v}' = d\bar{v}/dn$, and $K = z \exp(-\epsilon/k_B T)$.

In this paper, I am interested only in the case of constant α , corresponding to \bar{N}_o increasing in proportion to N . This gives

$$\bar{v} = (1 - \alpha)n, \quad \bar{v}' = 1 - \alpha.$$

The substitution of these values in equation (2) gives

$$z \exp\left(\frac{\mu - \epsilon}{k_B T}\right) = \frac{n}{(1 + \alpha n)^\alpha (1 - (1 - \alpha)n)^{1-\alpha}}. \quad (3)$$

Defining $x = z \exp((\mu - \epsilon)/k_B T)$ equation (3) becomes

$$\begin{aligned} x &= \frac{n}{(1 + \alpha n)^\alpha (1 - (1 - \alpha)n)^{1-\alpha}} \\ &=: f(n|\alpha). \end{aligned} \quad (4)$$

2. Occupation statistics

In the following, I shall consider the isothermal occupations which are generated by the different values of α .

Case $\alpha = 0$. For $\alpha = 0$, $f(n|\alpha)$ is given by

$$f(n|0) = n/(1 - n)$$

and is thus defined on the open interval $[0, 1)$, $\mathcal{D}_f = \{n : 0 \leq n < 1\}$. In this interval $f(n|0)$ ranges steadily with n from 0 for $n = 0$ to $+\infty$ for $n \rightarrow 1$. For all $x > 0$ equation (4) can thus be solved for n giving

$$n = \frac{1}{1 + 1/x} \quad (5)$$

$$= \frac{1}{\frac{1}{z} \exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1}. \quad (6)$$

Needless to say, equation (6) is nothing but the Fermi–Dirac occupation statistics.

Case $\alpha = 1$. For $\alpha = 1$, $f(n|\alpha)$ is given by

$$f(n|1) = n/(1 + n)$$

and is defined on the entire positive semiaxis $[0, +\infty)$, $\mathcal{D}_f = \{n : 0 \leq n < +\infty\}$. In this interval $f(n|1)$ ranges steadily with n from 0 for $n = 0$ to 1 for $n \rightarrow +\infty$. For $0 \leq x < 1$, equation (4) can thus be solved for n giving

$$n = \frac{1}{1/x - 1} \quad (7)$$

$$= \frac{1}{\frac{1}{z} \exp\left(\frac{\epsilon - \mu}{k_B T}\right) - 1} \quad (8)$$

Needless to say, equation (8) is the Bose–Einstein occupation statistics.

Case $-\infty < \alpha < 1$. Excepting a few special cases, for $-\infty < \alpha < 1$ equation (4) cannot be solved for n in closed form. To get qualitative information on the solution, observe first that in general $f(n|\alpha)$ is defined only for $0 \leq n < 1/(1 - \alpha)$, $\mathcal{D}_f = \{n : 0 \leq n < 1/(1 + \alpha)\}$, where varies from 0 for $n = 0$ to $+\infty$ for $n \rightarrow 1/(1 + \alpha)_-$. Thus, for each x equation (4) admits a unique solution $n(x)$. The asymptotic behaviours of this function are given by

$$\begin{aligned} x \rightarrow 0 &\implies n \sim x, \\ x \rightarrow +\infty &\implies n \rightarrow 1/(1 - \alpha). \end{aligned}$$

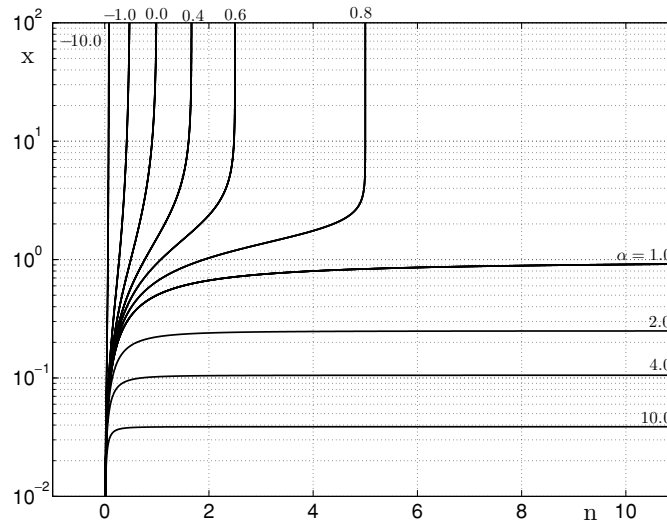


Figure 1. Log-linear plot of $z \exp((\mu - \epsilon)/k_B T)$ versus the occupation probability n for a few values of the parameter α in the interval $-10 \leq \alpha \leq 10$.

In a few selected cases explicit solutions can, however, be found. For instance, for $\alpha = -1$ the isotherm is given by $n = \frac{1}{2} (1 - \sqrt{1 - 4x/(1 + 4x)})$.

Case $1 < \alpha$. For $\alpha > 1$, $f(n|\alpha)$ is conveniently written as

$$f(n|\alpha) = n(1 + (\alpha - 1)n)^{\alpha-1} / (1 + \alpha n)^\alpha.$$

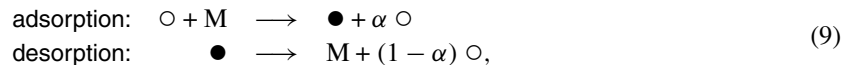
This function is defined for $0 \leq n < +\infty$, $\mathcal{D}_f = \{n : 0 \leq n < +\infty\}$, where varies from 0 for $n = 0$ to $(\alpha - 1)^{\alpha-1} / \alpha^\alpha$ for $n \rightarrow +\infty$. Thus, equation (4) can be solved for n only for $0 \leq x < (\alpha - 1)^{\alpha-1} / \alpha^\alpha < 1$, and the solution has the following asymptotic behaviours:

$$\begin{aligned} x \rightarrow 0 &\implies n \sim x, \\ x \rightarrow \frac{(\alpha - 1)^{\alpha-1}}{\alpha^\alpha} &\implies n \rightarrow +\infty. \end{aligned}$$

From the above discussion it follows that for any α , with $\alpha < 1$, the domain \mathcal{D}_f is unlimited and the function is therein bounded, while for any α , with $\alpha \geq 1$, the domain \mathcal{D}_f of $f(n|\alpha)$ is limited and the function diverges at the border. Moreover, the family $\mathcal{F} = \{f(n|\alpha) : -\infty < \alpha < 1\}$ of curves has as envelop the line $x = n$ which is not a member of the family. Considered as function of the parameter, the family \mathcal{F} undergoes a catastrophe at $\alpha = 1$. Figure 1, showing $f(n|\alpha)$ for a few values of α , sketches the above results.

3. Application to adsorption–desorption phenomena

Observe now that adsorption–desorption (collectively referred to as ADsorption) processes can to a large extent be described by processes A and D,



provided that \circ and \bullet are identified with empty and filled sites, respectively, and M is the adsorbed molecule.

This scheme was proposed by Cerofolini (developing an idea originally formulated by Landsberg [5]) as an extension of Langmuir theory accounting for ADSorption-induced reconstruction [6, 7]. The theory was developed on *kinetic* bases, assuming that the reaction rates are described by the mass-action law.

Does the fractional *statistical* description apply to the same phenomena? To give an answer to this question, we observe that surface reconstruction necessarily involves some changes in the internal energy of the system—that would imply that the internal energy of the system varies with N_o . Since in section 1 the internal energy of the system was assumed to vary as ϵN , the fractional statistical theory therein developed cannot be applied to the description of ADSorption-induced reconstruction. Rather, it can be applied to the description of ADSorption where the entire exchanged energy is that involved in ADSorption events.

Since the case of ADSorption-induced reconstruction is excluded, $N_o(0)$ must necessarily be regarded as the number of adsorption sites N_s at the surface. Accepting this interpretation, $n (= N/N_o(0) = N/N_s)$ may tentatively be assumed to be the surface coverage θ . The graphs in figure 1 show, however, that only in one case ($\alpha = 0$) n saturates to 1 for $x \rightarrow +\infty$. For $\alpha < 0$, n saturates to values lower than unity; for $\alpha > 0$, n either saturates to values higher than unity $x \rightarrow +\infty$ or diverges at finite x . These occurrences strongly suggest that the fractional statistical theory developed describes either multisite occupation (for $\alpha < 0$) or multilayer ADSorption ($\alpha > 0$).

The application of the above results requires that the chemical potential is specified. If the adsorbed phase is in contact with a gas with chemical potential μ_g , the equilibrium condition gives $\mu = \mu_g$. For an ideal gas at pressure p , the chemical potential of μ_g is given by

$$\mu_g = k_B T \ln(p/p_g)$$

with p_g a characteristic pressure related to the internal partition function in gas phase. Equation (4) determines thus the isothermal occupation of the adsorbed phase as a function of gas pressure:

$$p/p_0 = \frac{n}{(1 + \alpha n)^\alpha (1 - (1 - \alpha)n)^{1-\alpha}}, \quad (10)$$

where $p_0 = (p_g/z) \exp(\epsilon/k_B T)$.

The application of the above considerations to ADSorption equilibrium (9) is summarized in the following:

1. For $\alpha = 0$, equation (10) is nothing but the Langmuir isotherm.
2. The interpretation of equation (10) in terms of multilayer adsorption requires additionally that
 - (i) the average height n^* of the adsorbed film is given by $n^* = 1 + n$ (because the originally empty sites belong to adsorbed molecules and thus contribute to the film height), and
 - (ii) the formation of the first layer is described by the Langmuir isotherm, though with a different characteristic pressure p_L (because the internal partition function at the surface and in upper layers may be different).

Accepting these stipulations, for $\alpha = 1$ the mean surface coverage θ is given by

$$\theta = \frac{Cp/p_0}{1 + Cp/p_0} \frac{1}{1 - p/p_0},$$

where $C = p_0/p_L$. This isotherm, which from the statistical point of view corresponds to the adsorption of fermions on the first layer and bosons in upper layers, is strongly reminiscent of the Brunauer–Emmett–Teller isotherm [8],

$$\theta_{\text{BET}} = \frac{Cp/p_0}{1 + (C - 1)p/p_0} \frac{1}{1 - p/p_0}.$$

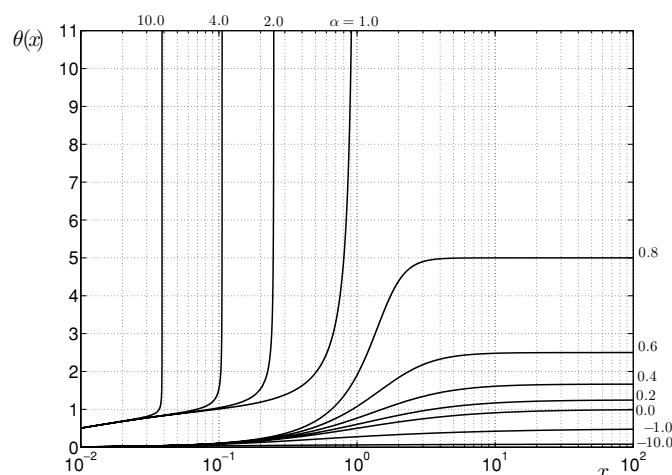


Figure 2. Linear-logarithmic plot of the Adsorption isotherm versus gas pressure for a few values of the parameter α in the interval $-10 \leq \alpha \leq 10$ calculated assuming $C = 100$.

3. Case $\alpha < 0$ was applied by Riccardo *et al* to the adsorption of polyatomic molecules responsible for the exclusion of additional sites with respect to those directly involved in the adsorption [9], for which it was found to provide consistent results with Monte Carlo simulations.
4. Case $0 < \alpha < 1$ may be applied to multilayer Adsorption, where the adsorption in an upper layer occurs on the top of α^{-1} underlying molecules. Transforming n in θ , however, requires the same correction as considered in item 2.
5. Case $\alpha > 1$ may be applied to the adsorption of dendrimers or to multilayer Adsorption with branching piles.

Figure 2 shows the Adsorption isotherms corresponding to the cases shown in figure 1 in the hypothesis that all cases with $\alpha < 1$ apply to submonolayer Adsorption while cases with $\alpha \geq 1$ apply to multilayer Adsorption.

4. Conclusions

In this work I have shown how a fractional statistical analysis of equilibrium (1) with constant α is able to account for a few situations occurring in Adsorption, such as the exclusion from adsorption of unoccupied sites, multilayer adsorption with branching and dendrimer growth, in addition to the canonical Langmuir and BET isotherms observed in submonolayer and multilayer adsorption, respectively. Dropping the condition on the constancy of α is expected to be able to account for other phenomena such as adsorption-induced defractalization [10], roughness-induced wetting [11], protein unfolding during the adsorption of polar molecules [12], and adsorption in restricted geometries, with only modest complications of the description.

References

- [1] Haldane F D 1991 *Phys. Rev. Lett.* **67** 937
- [2] Murthy M V N and Shankar R 1994 *Phys. Rev. Lett.* **72** 3629

- [3] Wu Y-S 1994 *Phys. Rev. Lett.* **73** 922
- [4] Isakov S B 1994 *Phys. Rev. Lett.* **73** 2150
- [5] Landsberg P T 1955 *J. Chem. Phys.* **23** 1079
- [6] Cerofolini G F 2003 *Phys. Rev. E* **67** 041603
- [7] Cerofolini G F 2003 *J. Chem. Phys.* **118** 10203
- [8] Steele W A 1975 *The Interaction of Gases with Solid Surfaces* (Oxford: Pergamon)
- [9] Riccardo J L, Ramirez-Pastor A J and Romá F 2004 *Phys. Rev. Lett.* **93** 186101
- [10] Pfeifer P, Wu Y J, Cole M W and Krim J 1989 *Phys. Rev. Lett.* **62** 1997
- [11] Netz R R and Andelman D 1997 *Phys. Rev. E* **55** 687
- [12] Cerofolini G F 1997 *Langmuir* **13** 995