General Cluster Sorption Isotherm

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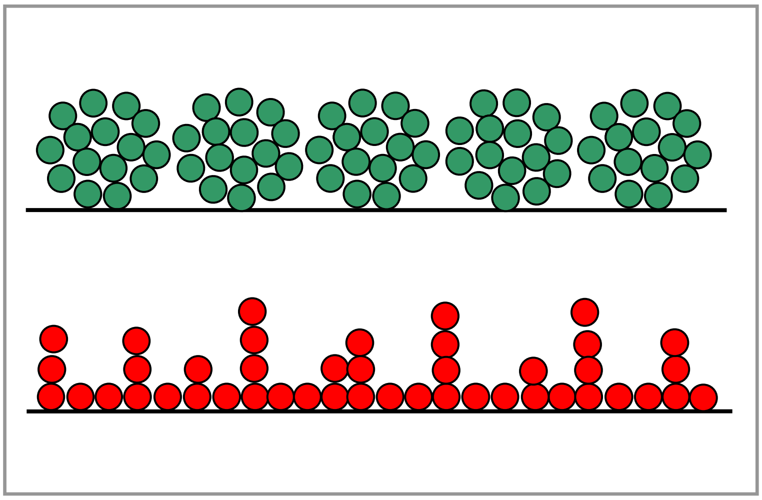

Summary

Adsorption isotherms are an essential tool in chemical physics of surfaces. However, several approaches based on a different theoretical basis exist and for isotherms including capillary condensation existing approaches can fail. Here, a general isotherm equation is derived and applied to literature data both concerning type IV isotherms of argon and nitrogen in ordered mesoporous silica, and type II isotherms of disordered macroporous silica. The new isotherm covers the full range of partial pressure (10^{-6} - 0.7). It relies firstly on the classical thermodynamics of cluster formation, secondly on a relationship defining the free energy during the increase of the cluster size. That equation replaces the Lennard-Jones potentials used in the classical density functional theory. The determination of surface areas is not possible by this isotherm because the cross-sectional area of a cluster is unknown. Based on the full description of type IV isotherms, most known isotherms are accessible by respective simplifications.

Keywords: modeling; adsorption isotherm; argon; nitrogen; ordered mesoporous silica; MCM-41; nonporous silica; NLDFT; QSDFT

1. Introduction

A sorption isotherm is the result of molecular interaction between individual molecules with a surface and with these adsorbed molecules among each other. Traditionally, sorbate-sorbate interactions are described by lateral forces or multilayer formation[1]. More general and elegant is the concept of 3-dimensional clusters which can merge and form a surface attached liquid film or fill the confined space of mesopores[2].[3] The resulting isotherm of mesopore-filling has a sigmoidal shape and is known as type IV in the UPAC classification[4]. It can be regarded as the most complex isotherm comprising all known other isotherms as respective simplifications. That complexity is only outreached by the existence of several distinct adsorption sites on the surface. Since that heterogeneity is commonly treated as an only additive superposition of homogeneous patches[5] [6], the focus of the present article is limited to homogeneous sorbents.

Here we concentrate on subsequent processes starting with the adsorption of low concentrated and isolated molecules on an ideal plane surface via clustering to capillary condensation. These isotherms are of special interest for the determination of pore size distributions by sorption of argon or nitrogen at their boiling temperature. Modern methods rely on the classical density functional theory (DFT) which is here employed to statistical mechanics.[7] The adsorbate molecules are simplified as hard spheres in front of the rigid adsorbent surface. Liquid-solid interaction is modeled by two parameters of a Lennard-Jones (LJ) potential resulting from fitting to non-porous surfaces while the LJ potential of the liquid-liquid interaction is defined by a fit procedure to isotherms for ordered mesoporous materials with defined pore diameters.[7] Recent DFT versions are extended by an excess hard sphere attractive term. The non-local density functional theory (NLDFT) consists of an additional "smooth density approximation"[8], while the quenched solid density functional theory (QSDFT) formally treats the solid surface as a mixture of a solid and a fluid leading to a characteristic solid density profile[9]. These methods do not only allow the determination of pore sizes: modeling of adsorption isotherm is accomplished, too. However, NLDFT isotherms do only roughly follow the experimental basis; they are characterized by artificial steps.[7] QSDFT isotherms reproduce the experiment much better [10] [11] [12] but a significant deviation can occur in the very low pressure region[9].

Beside this sophisticated modeling simpler isotherms exist for sigmoidal isotherms. Semi-empirical approaches are reviewed [3] [13] and extended by a new contribution[14]. A recently proposed cluster formation model[3] stems from biochemistry. It is based on the thermodynamic equilibrium of multiple ligand-receptor complexes introduced by Klotz[15] and lastly has its root in the Langmuir-analog Michaelis-Menten[16] [17] concept. It was assumed in the cluster formation model[3] that the primary sorption step, necessary for the final clustering, can be described by only one parameter. When S is the a primary binding site on the adsorbent A, the multi-site binding is described by

$$S + A \leftrightarrow SA\;; \qquad SA + A \leftrightarrow SA_2\;; \qquad SA_2 + A \leftrightarrow SA_3$$

and so on. Based on this successive thermodynamical equilibrium a *ß*-fold clustering with the primary sorption constant K_1 and the cluster formation constant K is established, and the degree of coverage θ as a function of the partial pressure x is derived[3] to be

$$(1) \qquad \theta = \frac{C_1\,(Kx)\left\{1-(1+\beta)\,(Kx)^{\beta}+\beta\,(Kx)^{\beta+1}\right\}}{\left(1-(Kx)\right)\left\{1+\left(C_1-1\right)(Kx)-C_1\,(Kx)^{\beta+1}\right\}}$$

where C_1 is given by

$$(2) \qquad C_1 = K_1 / K$$

That equation is identical with the ζ-isotherm of Ward et al.[18] derived by statistical thermodynamics.

Equation (1) was found to describe numerous type IV and V experimental isotherms[3]. However, its validity is restricted to a special case of type IV adsorption where the interaction with the pore walls is extremely weak or restricted to few defect regions whereas the adsorbate self-interaction is high. A prominent example is the adsorption of water in hydrophobic microporous carbon[2]. However, the application of equation (1) fails drastically for a lot of type IV isotherms, especially in case of the very important adsorption on ordered mesoporous materials. An example is shown in the Supplementary Information (SI) in Figure S1. To solve that problem a more general version of equation (1) with more degree of freedom is presented hereinafter.

2. Methods

All experimental data stem from the literature. Calculations were performed either by Excel or SigmaPlot software for curve fitting by nonlinear regression according to the

Levenberg-Marquardt algorithm[19]. To avoid the calculation with $\beta \to \infty$, β = 200 was fixed at 200 as a good approximation. The nonlinear regressions were performed with reciprocal weight of the processed adsorption values. Depending on the experimental data the numbers of the power functions, occurring during intermediate states of the regression program, can exceed the common limits of 10^{-300} and 10^{+300}. This had to be considered during programming. The optimization of the natural numbers of α was done manually.

3. Results and Discussion

3.1. Type IV isotherms

Recurring to the general Klotz isotherm[15] the degree of adsorption θ, defined as the adsorbed amount per monolayer and ranging from 0 to β, is defined by a quotient of two geometric series

$$(3) \qquad \theta = \frac{K_1\, x + 2\, K_1\, K_2\, x^2 + 3\, K_1\, K_2\, K_3\, x^3 + \ldots\ldots + \beta\,(K_1\, K_2\, K_3 \ldots\ldots K_i)\, x^\beta}{1 + K_1\, x + K_1\, K_2\, x^2 + K_1\, K_2\, K_3\, x^3 + \ldots\ldots + (K_1\, K_2\, K_3\ \ldots\ldots K_i)\, x^\beta}$$

where x is the partial pressure and the constants K_i define the different ligand-receptor equilibria. When the products of K_i are defined by

$$(4) \qquad C_i = \frac{1}{K} \prod_{i=1}^{i} K_i$$

and q is introduced by

$$(5) \qquad q = K\, x$$

eqn. (3) can be written as

$$(6) \qquad \theta = \frac{\sum_{i=1}^{\beta} i\, C_i\, q^i}{1 + \sum_{i=1}^{ß} C_i\, q^i}$$

This description of a general multiple equilibrium is transferred to a capillary condensation process. In the foregoing publication[3] the adsorption on the primary sites was assumed to be defined only by K_1, and all other constants from K_2 to K_β are responsible for the clustering. In that case all values of K_i beside K_1 are equal and given by K. Here it is assumed that the primary sorption is defined not only by C_1 but by C-values ranging from C_1 to C_α. The following transformations aim at the separation of the geometric series in one with different C values ranging from C_1 to C_α, and another with equal $C = 1$. At first the numerator of eqn. (6) is considered and split into

$$\sum_{i=1}^{\beta} i\,C_i\,q^i = \sum_{i=1}^{\alpha} i\,C_i\,q^i + C_\alpha \sum_{i=\alpha+1}^{\beta} i\,q^i \tag{7}$$

The last term can be transformed to[20]

$$\sum_{i=\alpha+1}^{\beta} i\,q^i = \sum_{i=1}^{\beta} i\,q^i - \sum_{i=1}^{\alpha} i\,q^i = \tag{8}$$

$$= \frac{q\left(1-(\beta+1)q^{\beta} + \beta\,q^{\beta+1}\right)}{(1-q)^2} - \frac{q\left(1-(\alpha+1)q^{\alpha} + \alpha\,q^{\alpha+1}\right)}{(1-q)^2}$$

$$= \frac{q\left((\alpha+1)q^{\alpha} - (\beta+1)q^{\beta} + \beta\,q^{\beta+1} - \alpha\,q^{\alpha+1}\right)}{(1-q)^2}$$

The denominator of eqn. (6) is split into

$$1 + \sum_{i=1}^{\beta} C_i\,q^i = 1 + \sum_{i=1}^{\alpha} C_i\,q^i + C_\alpha \sum_{i=\alpha+1}^{\beta} q^i \tag{9}$$

The last term can be transformed to[21]

$$\sum_{i=\alpha+1}^{\beta} q^i = \sum_{i=1}^{\beta} q^i - \sum_{i=1}^{\alpha} q^i = \frac{q-q^{\beta+1}}{1-q} - \frac{q-q^{\alpha+1}}{1-q} = \frac{q^{\alpha+1}-q^{\beta+1}}{1-q} \tag{10}$$

Based on the foregoing equations the full hybrid isotherm is

$$\theta = \frac{\displaystyle\sum_{i=1}^{\alpha} i\,C_i\,q^i + \frac{q\,C_\alpha\left((\alpha+1)q^{\alpha} - (\beta+1)q^{\beta} + \beta\,q^{\beta+1} - \alpha\,q^{\alpha+1}\right)}{(1-q)^2}}{\displaystyle 1 + \sum_{i=1}^{\alpha} C_i\,q^i + C_\alpha \frac{q^{\alpha+1}-q^{\beta+1}}{1-q}} \tag{11}$$

or

$$\theta = \frac{\displaystyle (1-q)^2 \sum_{i=1}^{\alpha} i\,C_i\,q^i + q\,C_\alpha\left((\alpha+1)q^{\alpha} - (\beta+1)q^{\beta} + \beta\,q^{\beta+1} - \alpha\,q^{\alpha+1}\right)}{\displaystyle (1-q)^2\left(1 + \sum_{i=1}^{\alpha} C_i\,q^i\right) + (1-q)\,C_\alpha\left(q^{\alpha+1}-q^{\beta+1}\right)} \tag{12}$$

In principle, that isotherm can be used to fit experimental results. However, convergence is seldom achieved when the number α is greater than 5. An example

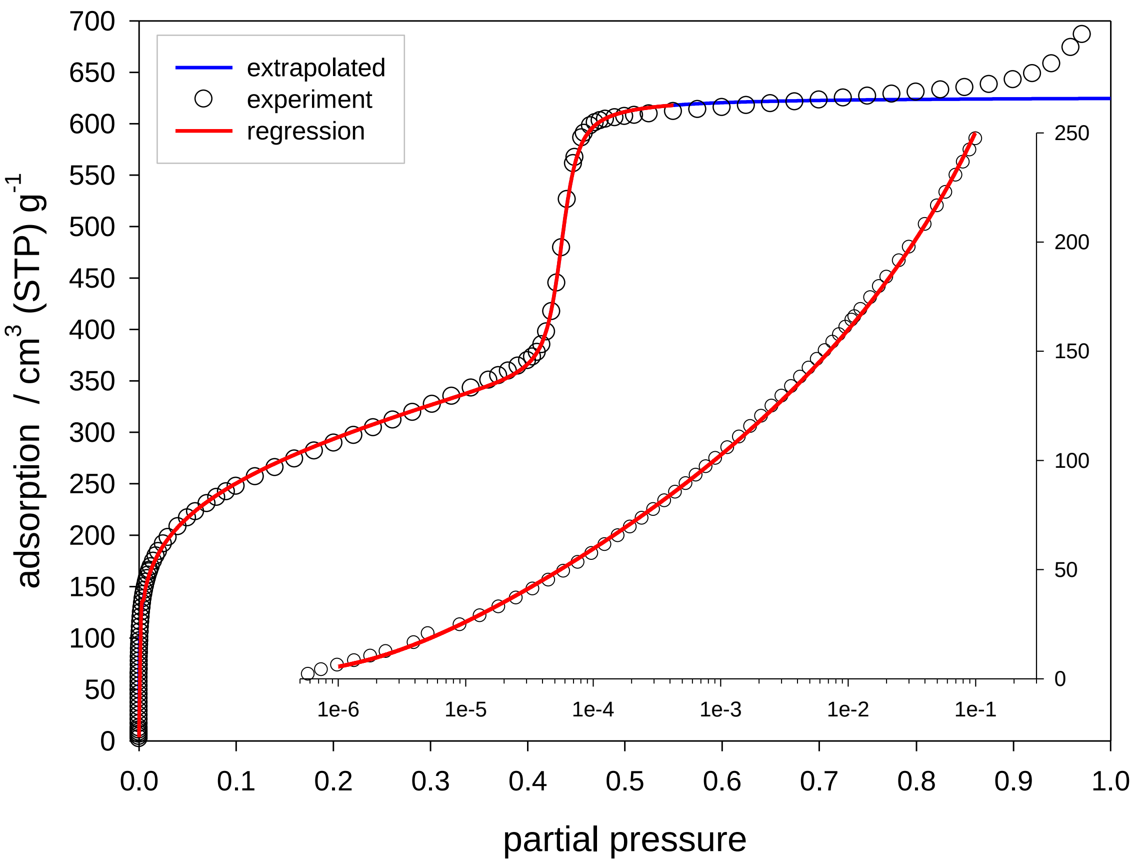

Figure 1: Application of the General Cluster Sorption Isotherm (eqn. (12) with boundary conditions (15,16) to the adsorption of nitrogen (77 K) on siliceous MCM-41 (pore diameter 4.5 nm). Regression from $x = 10^{-6}$ up to 0.6, extrapolated to $x = 1$. Data taken from[24] (supporting information)

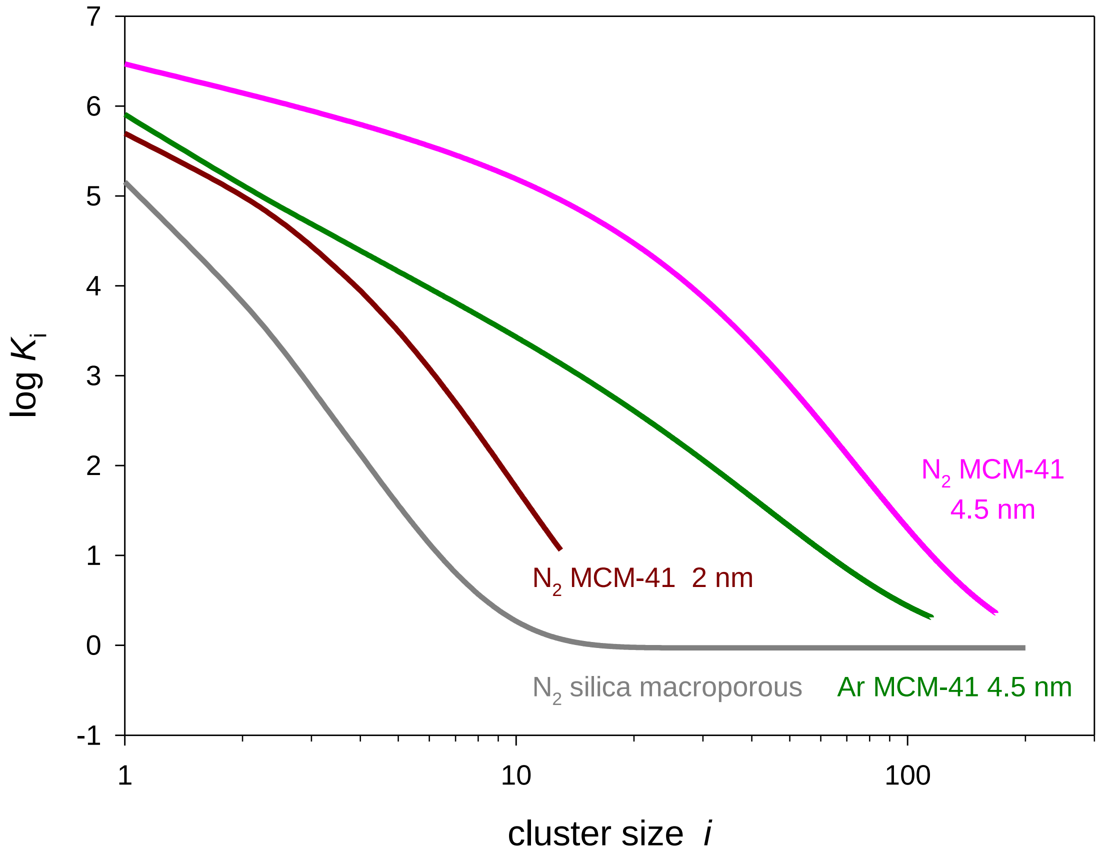

Figure 2: Relative incremental free energy log K_i as a function of the cluster size i.

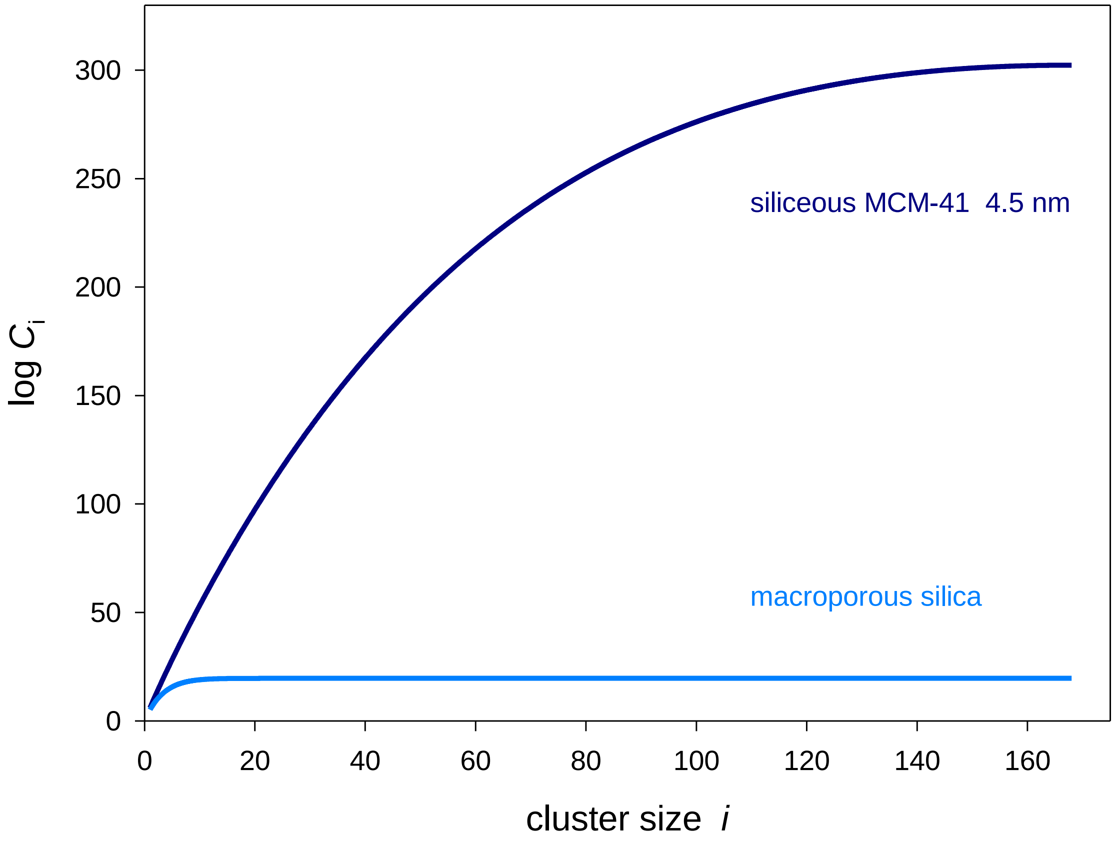

Figure 3: Relative integral free energy log K_i as a function of the cluster size i.

is presented in the SI (Figure S2). The resulting values of C_i were found to decrease with increasing i, which prompts the existence of a general function relating C_i to each other. Instead of further considering C_i the problem is shift to the equilibrium constants K_i which define C_i via the product series given in eqn. (4). The Ki values define a respective energy

(13) $\varepsilon(i) = kT \ln (K_i / K_o)$

with the scaling factor K_o. This energy should depend on the position of the clusters in front of the adsorbent surface and its size i. Respective equations found in the literature are based on power laws of inter particle or particle-surface distance, commonly known as LJ potentials. They play a central role in the classical DFT[7] and are also used in the modeling of adsorbed clusters[22]. Instead, the energy as a function of solely the molecules number i inside a cluster is required here. Since no equation was found in the literature, it was tried whether power functions of i are able to describe experimental type IV isotherms. Intuitively chosen combinations of power laws and their test in fitting of theory and experiment have revealed the following energy function

(14) $\varepsilon(i) = \varepsilon_o\, i^{-a} (i^{-b})^{i}$

ε_0 is the energy when no cluster is present (i = 0). The first term i^{-a} may be interpreted as the energy of the entire cluster in front of the adsorbent surface. Most fittings with experimental data have yielded $a > 0$ meaning that the cluster energy decreases with increasing cluster size. When the cluster is bigger the mass center is assumed to have a larger distance, thus reflecting a lower attractive LJ potential. To come to the energy for the addition of one adsorbate molecule to one of the cluster molecules the cluster energy i^{-a} is multiplied with the sorbate-sorbate interaction energies of each cluster molecule (i^{-b}) or $(i^{-b})^{i}$ for the entire cluster, so that. the energy decreases with i and increasing b > 0. This interpretation is only very rough. Quantum mechanically DFT modeling[22] [23] or Grand Canonical Monte Carlo simulation[23] may close the gap between the empirical energy-cluster size relationship (14) and the present theoretical background.

By combining equation (13) and (14) one obtains

(15) $K_i = K_o \exp \{ \varepsilon_0/kT) \, i^{-(a + bi)} \}$

Based on equations (12) and (15) a respective program for nonlinear regression has been written. The tested experimental data concerns the adsorption isotherm of nitrogen in ordered mesoporous silica of the type MCM-41.[24] That type of material consists of cylindrical pores with a tight pore size distribution[24] and can therefore be regarded as homogeneous, a condition which is very important for the validation of the theoretical background. of the isotherm. Figure 1 shows the good fit beginning at relative pressures of 10^{-6} up to 0.7 including the steep increase at the relative pressure of 0.35 caused by capillary condensation. The positive deviation at higher pressure is due an additional secondary mesopore system which cannot be avoided by the synthesis conditions[24]. A very important observation is that the scaling factor K_o merges with K_α and K which is the point where the capillary condensation proceeds. Therefore, K_o is not necessary a free parameter but should be defined by

(16) $K_o = K = K_\alpha$

for this isotherm type. The observed fit of the theoretical isotherm is much better than that attainable by NLDFT[7]. It can be compared with the accuracy of QSDFT isotherms[10] [11] [12].

Figure 2 shows the course of K_i as a function of the cluster size i. Starting at K_1 the decrease is very strong and ends with $K = K_\alpha$. Note the logarithmic scale for K

indicating that it is a measure of the free energy contribution of the step from i - 1 to i. The course of log C_i defined in equation (4), which is nothing else than the cumulated relative free energy up to i, is shown in Figure 3. It is a hyperbolic function.

While the MCM-41 discussed above has 4.5 nm wide pores[24], another MCM with only 2.0 nm was also investigated for nitrogen adsorption[25]. The excellent fit between theory and experiment is shown in the SI (Figure S3). Here the expected sharp increase caused by capillary condensation is nearly invisible. But the application of the new isotherm can resolve its existence.

The nitrogen isotherms were recorded at its boiling point at 77 K. Another example shown in the SI (Figure S4) concerns the adsorption of argon at 77 K[26] which is a liquid in inside the 4.5 nm wide pore[27] at this temperature although its bulk phase melting point is 84 K.

Table 1: Parameters of the General Cluster Sorption Isotherm for type IV isotherms (eqn. 12, 15, 16) and type II isotherms (eqn. 17, 15, 18) as a result of its application to experimental isotherms from the literature[24 34 41]. K_1 and Q_o are calculated results. N is the number of experimental points used for regression and R the regression coefficient. *) No parameter but arbitrarily chosen values (see text).

adsorbent		K_1	K	ε_o / kT	a	b	α	β	Q_o / cm^3 (STP) g^{-1}	N	R
MCM-41, 4.5 nm	N_2 77K	2.94E+06	2.298 ± 0.002	15.1332 ± 0.12	6.73E-02 ± 2.8E-03	2.70E-03 ± 5.5E-05	168	287.6 ± 1.30	626.2 ± 1.8	95	0.999876
MCM-41, 2.0 nm	N_2 77K	4.97E+05	11.468 ± 0.133	14.1863 ± 0.28	1.06E-01 ± 3.5E-03	3.37E-02 ± 1.8E-03	13	16.3 ± 0.08	198.1 ± 0.2	80	0.999979
MCM-41, 4.5 nm	Ar 77K	8.08E+05	2.053 ± 0.002	13.5928 ± 0.16	2.00E-01 ± 4.4E-03	3.67E-03 ± 1.1E-04	115	226.4 ± 1.04	784.4 ± 2.7	115	0.999907
macroporous silica	N_2 77K	3.10E+05	0.967 ± 0.003	12.68 ± 0.13	1.84E-01 ± 7.2E-03	5.50E-02 ± 5.1E-03	200*		0.646 ± 0.044	102	0.999741
macroporous silica	Ar 87K	1.29E+04	0.993 ± 0.001	9.48 ± 0.11	2.44E-01 ± 3.3E-03	8.60E-03 ± 6.0E-04	200*		0.193 ± 0.012	119	0.999919

The calculated parameters are listed in Table 1. Beside the real 6 model parameters the table also contains the absolute adsorption at the saturation state Q_o and the value of K_1 which is calculated based on ε_o and K.

3.2. Type II isotherms

We will now proceed with the application of the new concept to type II isotherms. Often the modeling of type II isotherms is limited in its range. The BET isotherm[28] is practically, in case of surface area evaluation, restricted to the pressure segment between 0.05 and 0.3[29]. More successful are the BET modification by Anderson[30] and the Frenkel-Halsey-Hill[1] equation. But in some cases, for example in the adsorption on macroporous silica, their application fails[31 32], and even the use of equation (1) of the preceding cluster model[3] proposed by Ward[33] yields deviating results. The strong error of the last three isotherms is demonstrated here for the adsorption of nitrogen on macroporous silica[34] (SI, Figure S5).

When the General Cluster Sorption Isotherm (eqn. (12) is applied to type II isotherms, the value of K defines the free energy of condensation $RT \ln K$ [3]. The position of K at the relative pressure axis of the isotherm is located at $x < 1$ for capillary condensation (type IV) but around $x = 1$ in the unlimited condensation of type II open systems. However, analyzing sorption isotherms in the region of x between 0.98 and 1.0 is impaired by a principal strong increase of the experimental error[35]. The occurrence of a metastable equilibrium[36] during the condensation and additional condensation within the interstitial space of the particle bed are further problems. Hence, the isotherm interpretation has to strongly rely on a theoretical basis. Both kinetic Monte-Carlo Simulation[36 37] and the theory of disjoining pressure[38] may help to understand that region. Ward et al.[33 39] assumed that the isotherm passes through a point of inflection near $x = 1$ and attains a hypothetical saturation value at $x > 1$. But I do not agree with that opinion and, in accordance with the BET theory[28], it is assumed here the absence of an inflection point. Hence, the power β must tend to reach infinite.

Let us look to equation (12). With $\beta \to \infty$ the two β containing terms in the numerator cancel and the $\beta-$term in the denominator disappears for $q < 1$.Hence the isotherm equation for type II is

$$(17) \quad \theta = \frac{(1-q)^2 \sum_{i=1}^{\alpha} i\, C_i\, q^i + q\, C_\alpha \left((\alpha+1) q^\alpha - \alpha\, q^{\alpha+1}\right)}{(1-q)^2 \left(1 + \sum_{i=1}^{\alpha} C_i\, q^i\right) + (1-q)\, C_\alpha\, q^{\alpha+1}}$$

Equation (15) defining the dependence of K_i on i remains. But nonlinear regression of several experimental data has shown that $K_0 \neq K_\alpha$ and that equation (16) is restricted to

$$(18) \quad K_0 = K$$

Characteristic for this application is that the nonlinear regression yields $\alpha \to \infty$ Thus, both α and β approximate infinite when the condensation at $x = K$ is being achieved. Figure 4 shows the application of that new isotherm to experimental data concerning the adsorption of nitrogen on macroporous silica[40]. While known isotherms fail (SI, Figure S5) an excellent fit is obtained here over a range of $x = 10^{-6}$ to 0.99. The course of the K_i values starting from K_1 down to K is shown in the SI. Another example, presented here, concerns the adsorption of argon (87 K) on the same

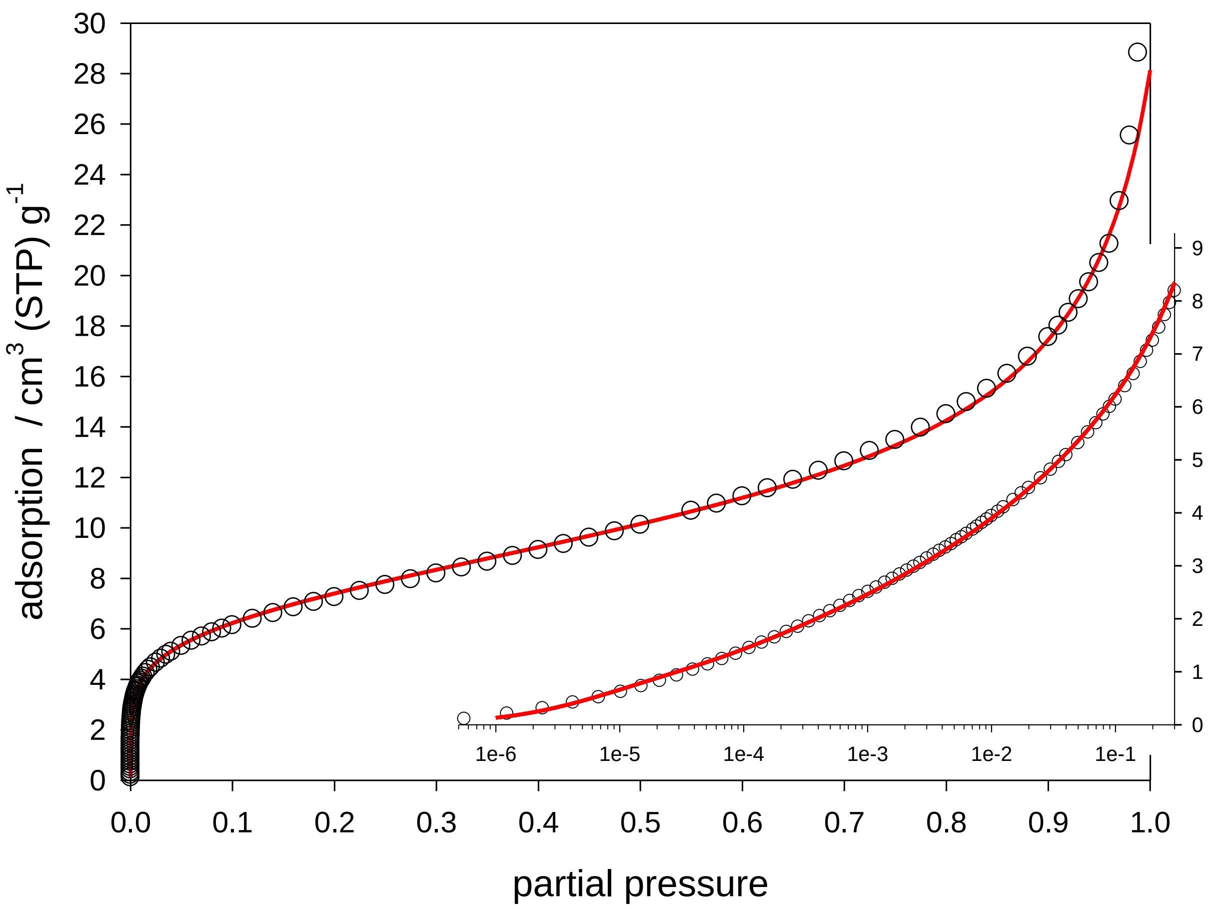

Figure 4: Application of the General Cluster Sorption Isotherm (eqn. (17) with the boundary conditions (15,18) to the adsorption of nitrogen (77 K) on macroporous silica[40].

silica[41]. The isotherm fit is shown in the SI (Figure S6) and the resulting parameters are presented in Table 1. Important is that the General Cluster Sorption Isotherm is only conditionally congruent with the BET-multilayer concept. The BET fit in the region between x = 0.05 - 0.20 yields Q_o = 5.92 cm^3 (STP) g^{-1} for the adsorption of nitrogen and Q_o = 5.23 cm^3 (STP) g^{-1} for argon while the respective results of the General Cluster Sorption Isotherm are 0.65 and 0.19 cm^3 (STP) g^{-1}. The most reasonable explanation is that the cross-sectional area of the adsorbed cluster is significantly greater than that of a single molecule. The formal cross-sectional area of the nitrogen cluster is therefore 8.0 times larger than that of the N_2 molecule and 27.5 times larger than that of the argon single molecule. The BET concept is based on the simplifying assumption of only vertical layer-to-layer interactions, so that the area of the stacked layers is given by the constant area required by one molecule. In contrast, the space requirement of a cluster is undefined because of its unknown geometry. The geometry should be a result of the balance between spherical sorbate-sorbate interactions and unidirectional sorbate-surface forces. At this point it has to be kept in mind that the adsorption of clusters is a formal concept. One cannot conclude that the clusters have to be separated from each other. Thus layers may be formed according to the common imagination[42]. The graphical abstract in front of this paper is therefore only formally correct.

For clarity a comment has to be added regarding the definition of the degree of coverage used in this article. In case of the type IV isotherm it is given by

(19) $\theta = Q \ / Q_o / \beta$

so that θ is unity at the adsorption saturation. But since β is canceled in case of type II isotherms (cf. eqn. (17)), it is defined only by

(20) $\theta = Q \ / Q_o$.

and θ is unity when the "cluster-monolayer" is reached.

3.3. Other types of isotherms

Up to now the application of the General Cluster Sorption Isotherm to type IV and type II isotherms has been discussed. Since type V isotherms can by regarded as a special case of type IV ($K_1 < K$)[3] the new isotherm must by valid for type V, too. The analog holds for type III being a special case of type II. When the decrease of K_i is extremely strong, the isotherm equation (12) can be approximated by neglecting $i > 1$ and we obtain equation (1)[3] which has been introduced into the literature as ζ-isotherm[18]. This equation reduces to Anderson's BET modification[30] for $\beta \to \infty$, to the *n*-layer BET equation[28] when $K = 1$, or to the common BET[28] when $\beta \to \infty$ holds in addition. BET is reduced to Langmuir[43] for $K = 0$, and the highest degree of reduction is obtained when Henry's law is reached. A direct test by differentiation of equation (12) is presented in the SI.

Not yet mentioned are stepwise type VI isotherms. If not occurring as a result of an additive superposition of several distinct sites of adsorption, the interpretation of these isotherms to occur on homogeneous surface[44] [45] can be explained by the assumption of several phase transitions[46] [47]. This requires an extension of eqn.(12): In case of a 2-step VI isotherm after the first phase transition at α with $K = K_I$ a second occurs with $K = K_{II}$ at β up to the maximal clustering at γ.

An important special type II adsorption is micropore filling. If the present concept can also be applied there and replace the established Dubinin-Radushkevich[48] equation requires an extra discussion and is planned to be presented elsewhere.

4. Conclusion

The present contribution is an extension of a published concept[3] describing the influence of capillary condensation on adsorption isotherms. While the application of the latter concept is restricted to adsorbates highly interacting with itself but with low affinity to the surface, the General Custer Sorption Isotherm is successfully tested for those type IV isotherms where the earlier concept fails. Instead of describing the adsorbent-surface interaction with only one parameter, an energy relationship is introduced. Depending on the degree of cluster size *i* the surface-cluster interaction including the cluster formation energy is proportional to the product of *i*+1 power functions

$$\varepsilon_i \propto i^{-a} \times \left(i^{-b}\right)^i$$

This relationship serves as an alternative to molecular distance-based LJ potentials used in classical DFT concepts. Here, the cluster approach results in energy contributions which are multiplied with each other, while the focus on only single molecules in DFT engenders additive contributions. The resulting isotherms describe the adsorption of nitrogen and argon on two types of ordered mesoporous silica in the partial pressure range from 10^{-6} up to more than 0.7. The fit is better than that obtained by NLDFT and comparable with the accuracy of QSDFT isotherms. An application to further type IV adsorption data including the evaluation and interpretation of the specific model parameters is therefore of strong interest.

The General Cluster Sorption Isotherm can be reduced to a form without capillary condensation effect. The resulting equation, with a cluster size approximating infinity at a partial pressure near unity, describes type II isotherms. In contrast to BET and other multilayer isotherms, the present concept is found to be applicable to a wide partial pressure range from 10^{-6} to 1 in case of nitrogen and argon on macroporous silica. Also here the extension to other experimental data and the interpretation of the fit parameters are required to be presented in future studies.

The present concept is only formally based on clusters. It is not necessary that the clusters are separated from each other: they may merge and form layers or a pore filling liquid in case of capillary condensation. However, although the basic derivation of the BET equation is very similar to the mathematical way gone here, the cluster approach is not fully equivalent to the established model of multilayers because the definition of a monolayer is missing in the present view. Only applying both concepts together allows the calculation of the cluster size forming a monolayer.

Since type IV isotherms can principally be reduced (or extended) to all other types of isotherms, the present concept seems to be universal. However, it is restricted to homogeneous systems. On the other hand, each heterogeneous adsorption has to be regarded as an additive superposition of isotherms for homogeneous patches. Hence, based on Langmuir isotherms the mathematically integration of a set of different Langmuir isotherms can be compared with experimental data so that the nonlinear regression yields a characteristic energy distribution[6]. The transfer of that approach to cluster isotherms is surely possible but the number of fit parameters combined with the calculation of power series inside a large span between very small and very large numbers is expected to be a mathematical challenge.

Integration of several isotherms is also required for pore size calculations. The parameter *K*, marking the position of capillary condensation, has to depend on the pore diameter. The General Cluster Sorption Isotherm is therefore expected to be a principle basis for pore size determinations.

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