Moisture Adsorption in 3D Self-Similar Structures

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Zusammenfassung

Gemäß neuesten mikroskopischen Untersuchungen weisen die Porenstrukturen von Zement sowie die von einigen Zeoliten eine statistische Selbstähnlichkeit auf, die sich über mehrere Größenskalen erstreckt.

Ziel dieser Arbeit ist die Auswirkungen der Selbstähnlichkeit auf den Adsorptionsprozess zu untersuchen. Dabei werden die folgenden Annahmen gemacht:

1. Selbstähnliche Strukturen werden durch exakte 3D Prefraktalen modelliert um die für die Adsorption relevanten geometrischen Faktoren berechnen zu können; Als exakte 3D Strukturen werden der Mengersche-Schwamm (MS) und der Mengersche-Filter (MF) verwendet.
2. Der Adsorptionsprozess wird durch ein Lattice-Gas Model beschrieben, das die Kohesions- (Kohesionsenergie c) und Adhesionswechselwirkungen (Adhesionsenergie a) berücksichtigt und deren Parameter: a/c, a respektive c/kT den bauphysikalisch relevanten Bereich – Wasser bei Raumtemperatur – einschliessen.

Adsorptionsisothermen wurden danach entweder in geschlossener Form (bei kleinen Strukturen) oder durch Monte Carlo Simulationen (bei grösseren Strukturen) berechnet. Die Untersuchung der Abhängigkeit von geometrischen und energetischen Parametern hat zu den folgenden Schlussfolgerungen geführt:

- Falls die Kohesionsenergie Null ist (c = 0), hat die Porenstruktur und demzufolge auch die Selbstähnlichkeit keinerlei Einfluss auf die Adsorption. Die Isothermen hängen nur von der Verteilung der Adhesionsenergien ab und zeigen keine Stufen, anders als dies bei c > 0 der Fall ist.
- Bei c > 0 zeigen die zwei Strukturen MS und MF deutliche Unterschiede, wobei die folgenden zwei Komponenten eine wichtige Rolle spielen:
  a) Die Populationen von adsorbierten Molekülen, die entweder die gleiche Verbindungsenergie haben oder in der gleichen Porengeneration zu finden sind;
  b) Die Fähigkeit der Porenstruktur, die Aggregatbildung von adsorbierten Molekülen zu begünstigen;

1
Zusammenfassung

Die Porenstruktur des MS unterstützt die Aggregatbildung und führt zu Isothermen die durch sehr deutliche Stufen gekennzeichnet sind. Die Isothermen von MF dagegen sind glatt oder S-förmig und es sind keine Populationsstufen unterscheidbar. Mit der Einführung des Begriffes der „Kohäsionsfläche“ wurde versucht ein Mass für die Unterstützung der Aggregatbildung durch die geometrische Struktur zu definieren.

- Es hat sich gezeigt, dass die Selbstähnlichkeit bei Mikro- und Mesoporen, also für niedrige relative Feuchtigkeiten (hygroskopischer Bereich), einen wichtigen Einfluss auf die Adsorption hat. In den Makroporen (Kapillarbereich) dominieren dagegen die Volumeneffekte, und die Selbstähnlichkeit hat keine Bedeutung.

- Die wesentlichsten Phänomene spielen sich im Bereich $1 \leq a/c \leq 3$ ab. Bei $a/c=1$ zeigt die MS eine Füllung in aufsteigender Folge der Porengenerationen, die dann allmählich bei $a/c=3$ zu einer schichtweisen Adsorption übergeht. Die Isothermen der MF dagegen weisen eine geringe Abhängigkeit von $a/c$ auf: sie stellen einen Übergang von Typ III Isothermen ($a/c=1$) zu S-förmigen Isothermen ($a/c=3$) vor.


Die vorliegende Arbeit stellt eine Erweiterung von früheren Erkenntnissen basierend auf Oberflächenfraktalen auf exakte 3D selbstähnliche Strukturen dar. Verschiedene phänomenologische Adsorptionsmodelle sowie die Interpretation von experimentellen Adsorptionsisothermen konnten so verfeinert werden.
Abstract

Recent microscopic investigations have shown that hydrated Portland cement and also certain zeolites possess a statistically self-similar pore structure over several orders of magnitude, down to the micropore range.

The present work tries to analyze the consequences of self-similarity on adsorption in the frame of the following theoretical approach:

1. Statistically self-similar structures are modeled by exact 3D prefractals: the Menger-Sponge (MS) and the Menger-Filter (MF). This simplification of the pore structure makes an exact calculation of all geometric properties possible, which are relevant for adsorption.

2. The adsorption process is described by means of a lattice-gas model, which accounts both for adhesion (a) and cohesion (c) interactions. The parameters of the model are chosen in such a way as to mimic the adsorption of water vapor at room temperature, which is relevant in building physics.

Adsorption isotherms were obtained thereafter analytically (for small structures) or using Monte Carlo simulations (for large structures). The analysis of the dependence on various geometric and energetic parameters led to the following results:

- Provided the cohesion energy is zero (c = 0), the distribution of binding energies completely determines the isotherms, while the self-similarity has no effect at all. Thus, no stepwise isotherms can be observed, this would require c > 0.

- For c > 0, on the other hand, the structural differences between MS and MF manifest themselves in the isotherms. These differences can be reduced to the following key factors:
  a) The populations of molecules, which correspond to adsorption sites either of the same binding energy or those found in pores of the same size have a different spatial distribution in the two structures;
  b) This spatial distribution determines the ability of the pore structure to promote the building of aggregates of molecules belonging to the same population.

Accordingly, it has been shown that the MS promotes the building of aggregates, leading thereby to stepwise isotherms. The isotherms of the MF, however, are smooth.
Abstract

and S-shaped, such that no distinct populations can be deduced from the isotherms. In a first approach, the so-called cohesion boundary has been introduced in order to characterize the geometric feature of these adsorbents responsible for the building of aggregates.

• 3D self-similarity has an important influence on the adsorption isotherm mostly in the micro and mesopore range, i.e. at low pressures. In macropores, however, the volume effects dominate and the self-similarity has no importance.

• Concerning the dependence on the energetic parameters, the model shows a rich behavior in the range $1 \leq a/c \leq 3$. The isotherms of the MS undergo transitions from pore wise filling at $a/c=1$ to layer wise adsorption at $a/c=3$. In the same range, the MF shows a weaker dependence on $a/c$: Type III isotherms (at $a/c=1$) turn step by step to S-shaped isotherms (at $a/c=3$).

• The popular method for determining the so-called monolayer coverage: point B Method turned out to be misleading for several parameter ranges and the deviations from the real monolayer coverage could be quantified.

The novelty of the present work is that it extends previous studies made on self-similar surfaces to real 3D self-similar structures. As a result some phenomenological models and interpretations of experimental isotherms could be refined.
Chapter 1 Introduction

1.1 Self-similarity of porous materials

Many porous materials possess a large variety of pore sizes, ranging from nanometers to millimeters. In particular, the microscopic investigation of porous building materials (e.g., cement) shows a statistical self-similarity existing over many orders of magnitude. A piece of material when viewed by naked eyes (Fig 1.1) exhibits an apparently irregular pattern of pores and compact regions. The latter, when examined at higher resolution, reveals again a similar structure. Subsequent magnifications, limited from below by the molecular range, lead to similar patterns at different length scales.

One of the most fundamental processes in porous building materials is the adsorption of and the interaction with water molecules. The current interpretation of adsorption isotherms is based on very simple models of the pore structure [1]. This is represented either by slit-shaped pores, or by straight, cylindrical and non-connected pores with a given range of diameters.

Exact self-similarity is a basic property of mathematical fractals [2]. These offer a mean to model statistically self-similar porous materials. Following its introduction into physics [3], fractal geometry has become, in the latter two decades, a central concept of the physical chemistry of porous media [4]. At the beginning of this development Avnir and Pfeifer [5] have proposed to use the fractal dimension $D$ as a yardstick independent quantitative measure for the degree of surface irregularity (heterogeneity, roughness) of nanoporous materials. They illustrated this idea by performing BET surface area measurements of silicic acid using adsorbate molecules of different sizes. The authors deduced a fractal dimension of $D \approx 2.94$.
from the approximate scaling law between the measured surface area and the adsorbate molecule size (yardstick) used in the measurement.

The fractal approach was also used in order to describe the complicated microstructure of hydrated cement paste. Besides fractal dimensions derived from adsorption measurements [6], several other techniques as mercury intrusion porosimetry [7], image analysis [8, 9], scanning electron microscopy [10], transmission electron microscopy [11], small angle X-ray scattering [12, 13] and small angle neutron scattering [14, 15] brought evidence about the pseudofractal structure of hydrated cement paste.

Along with the accumulation of experimental data, also the fractal modeling of porous media showed an impressive development. A famous 3D fractal object, the Menger-Sponge has been mentioned by several authors [16-20] in relation to nanoporous materials. In his review paper [16] Rothschild gives a comprehensive presentation of the Menger-Sponge and describes the physio- and chemisorption on heterogeneous catalysts by use of fractal geometry. Other authors [17] discuss rigorously the extent to which ideal fractal networks like the Menger-Sponge may reflect the characteristics of real catalysts.

The classical BET [21] and the FHH [22-24] theories of adsorption were generalized to self-similar porous adsorbents [25] to establish a relation between the fractal dimension of the surface and adsorption isotherms. These studies were restricted, however, to so-called surface fractals, while real 3D fractals, the so-called mass-fractals, have not been investigated yet.

The present work tries to find out how far pure self-similarity can contribute to the understanding of real isotherms in mass-fractals. Self-similar porous media are modeled by regular 3D self-similar structures, obtained according to the generating algorithm of the Cantor-Set. The features of the pore structure are reduced to the minimum, and this has the advantage that any geometric quantity can be calculated exactly. Adsorption isotherms of these structures are obtained by means of Statistical Mechanics and Grand Canonical Monte Carlo simulations of a simple lattice-gas model of water. These isotherms are used in order to identify those features of the pore geometry, which are relevant for adsorption, and to determine the dependence of the adsorption processes on the energetic parameters.
1.2 Generalizations of the Cantor-Set to higher dimensions as models for self-similar porous bodies

1.2.1 The generating algorithm of the Cantor-Set

The Cantor-Set [2], the most simple 1D fractal, is defined by the following constructive procedure (Fig 1.2):

R1: take a segment of length 1;
R2: divide it in three equal parts;
R3: remove the middle part;
R4: apply the second and the third rule to the remaining parts repeatedly.

From the “initiator” \( CS_0 \) one obtains the first generation \( CS_1 \), the “generator” of the fractal, consisting of two subintervals. After \( n \) steps, \( CS_n \) is obtained, which is made up of \( 2^n \) subsegments of length \( 1/3^n \) each. The Cantor-Set is the collection of the “remaining” subsegments as \( n \to \infty \). This object is self-similar in that it contains copies of itself at many different scales: for each \( n > 0 \), \( CS_n \) can be expressed as the union of two subsets, each identical to \( CS_{n-1} \) up to a similarity transformation. The fractal dimension \( D \) [2] can be deduced from the scaling law of the minimum number \( N(l) \) of objects of given diameter \( l \) needed to cover the fractal, when the diameter \( l \) converges to zero:

\[
D = -\lim_{l \to 0} \frac{\ln N(l)}{\ln l}
\]  

(1.1)
For the Cantor-Set one obtains:

\[ D = \lim_{n \to \infty} \frac{\ln 2^n}{\ln 3^n} = \frac{\ln 2}{\ln 3} = 0.6309... \]  

(1.2)

1.2.2 Two-dimensional generalizations of the Cantor-Set

Using the generating algorithm of the Cantor-Set, higher dimensional fractal analogues are constructed. Here, the “middle part(s)” of the third rule R3, however, are not defined unequivocally, resulting in several possible analogues. In 2D these are the Cantor-Gasket (CG), Cantor-Tablecloth (CT) and Cantor-Cross (CC) (Fig 1.3) with fractal dimensions \( 1 < D < 2 \).

![Cantor-Fractals in 2D: prefractals of first and second generation](image)

1.2.3 Selection of the appropriate models from 3D generalizations

In 3D the number of regular Cantor type fractals is seven, corresponding to the possible combinations of three groups of middle parts: the single cube in the center (A), the six cubes in the middle of the faces (B) and the twelve cubes the middle of the edges (C). Accordingly, the seven generators in Fig 1.4. may be referred to as A, B, C, AB, AC, BC and ABC respectively. Among these only two generators, AB and AC, result in appropriate models for self-similar porous media, by satisfying the following conditions:

- a) whole pore space connected to the exterior or amount of closed pores negligible;
- b) mechanical stability of the solid body;
- c) interconnected pore space, offering possibilities to molecules to go across.
Generator AB corresponds to the **Menger-Sponge** ($MS$) fractal (Fig 1.5), which has been studied extensively as a model for nanoporous materials [16, 17, 26].

The fractal obtained from generator AC (Fig 1.6), the so-called **Menger-Filter** ($MF$), has not been previously mentioned in the literature and requires a more detailed description. The name refers to its physically relevant properties, as discussed further in section 1.3.1. The first generation prefractal $MF_1$ is obtained by removing a total of 13 smaller cubes from the initiator: 12 from the middle of the edges, and the single central cube, where the latter forms a closed pore. Starting from $MF_2$, however, the pore space becomes interconnected, offering ways for molecules to go across. This is illustrated by the intermediate state on Fig 1.6, where the smaller cube in the middle of the front face, signed by the arrow on $MF_1$, is not shown and the generator is applied to the five smaller cubes in the front only. All higher generation
prefractals possess closed pores: they are contained in the small building units identical to \( MF_1 \) up to a magnification. These represent only a negligible part of the pore space and in this thesis will be excluded from adsorption. Generator AC also leads to a relatively high surface area compared to the other generators.

As it will be seen in the following sections, these Cantor-Fractals represent two extremal porous bodies from the point of view of their topological and quantitative geometrical properties, as well as regarding the type of their adsorption isotherms. This makes them reasonable candidates for a classification of porous materials.
1.3 Geometric properties of the Menger-Sponge and Filter

1.3.1 Pore sizes and largest crossing particles

As seen in the previous section, the generating algorithm of both fractals consists of successive coring operations performed on the initiator cube of linear size $L$. At each step the size of the cubes to be removed is scaled down by a factor of three, such that the widths of successive pore generations form a geometric sequence (Appendix I). In reality this process is limited by the molecular structure of the material, which determines the size of the smallest pores as well as the generation $n$ of the prefractals. Therefore it is more convenient to index the pore generations according to their size starting with the smallest pores, such that one can refer to the latter without needing to specify the generation $n$ of the prefractals.

Although their pore sizes are identical, the two prefractals differ considerably in their transport properties, as explained below. These also justify the name Menger-Filter for the second fractal:

1. The largest spherical molecule, which can penetrate the Menger-Sponge, has a diameter of $L/3$. Correspondingly, the largest particle, which can be moved across the fractal, has a cross-section area of $L^2/9$;

2. In contrast, the Menger-Filter ($n \geq 2$) can be penetrated by spherical molecules of a maximal diameter of $L/9$ only. Due to the special pore structure, the largest particle, which can pass through, has a cross-section area of $L^2 \sqrt{2}/81$, i.e. somewhat larger than $(L/9)^2$. This largest cross-section amounts to only about 15.7% of the corresponding quantity of the Menger-Sponge.

3. Pore generations $k \geq 2$ of the Menger-Filter ($n \geq 2$) inherit the property described above under point 2. in the following way: certain regions of the $k^{th}$ pore generation can only be reached by molecules of size not exceeding $l_k/3$, where $l_k$ is the size of the $k^{th}$ pore generation. This is a consequence of the fact that larger pores are always separated by smaller constrictions.

4. In the Menger-Sponge, on the other hand, molecules of size $l_k$ can reach any pore of generation $k$. 
1.3.2 Porosity and surface area

Porosity and specific surface area are the most thoroughly studied properties of porous adsorbents [1]. The void fractions of most porous media lie in the range between 30% to 80% [17], while specific surface areas may be as large as $200 \text{m}^2/\text{g}$, as for hydrated cement [27]. From this point of view, real three-dimensional fractals represent a limiting case: they possess an infinite surface area and a porosity of 100%, that is, a vanishing volume. This justifies the introduction of the fractal dimension $D$ with $2 < D < 3$.

![Graph of porosity and specific surface area vs. prefractal generation](image)

**Fig 1.7** Dependence of a) porosity and b) specific surface area on the prefractal generation $n$; porosity is defined as the percentage of pore volume $V_n$ compared to the total volume $L^3$ of the adsorbent; specific surface area is given in units of $[\text{m}^2/\text{cm}^3]$ and is calculated for prefractals of size $L = 1 \text{\mu m}$.

The dependence of porosity and specific surface area on the prefractal generation $n$ has been studied based on the formulas in Appendix I. The results are shown in Fig 1.7:

1. The porosities of both structures converge to 100% as $n \to \infty$, the Filter showing a faster convergence: the void fraction of 83.5% of $MS_6$ already exceeds the porosity of most porous materials, while $MF_6$ shows a very high porosity of 98%, characteristic to certain aerogels only [17].

2. Specific surface areas in units of $\text{m}^2/\text{cm}^3$ have been calculated assuming $L = 1 \text{\mu m}$ for both structures. As seen in Fig 1.7 b) the surface area of the Menger-Sponge goes faster to infinity when $n \to \infty$. Specific surface areas of $MS_7$ ($543 \text{m}^2/\text{cm}^3$) and $MF_{10}$ ($462 \text{m}^2/\text{cm}^3$) are comparable to the measured values of $400 \text{m}^2/\text{cm}^3$ obtained for cement, assuming a density of $\rho = 2 \text{g/cm}^3$ [28].
1.3.3 Distribution of surface area and pore volume among pore generations

The volumes and surfaces related to pore generations $k = 1 \ldots n$ show the dependence typical for self-similar objects (see Appendix I). Surface areas decrease while pore volumes increase exponentially towards larger pore generations. Fig 1.8.

The distribution of surface areas among pore generations is similar in the two structures: Fig 1.8 a). For $n >> 1$ the smallest pores contain around 60% of the total internal surface. It must be reminded, however, that $MF_6$ has a total internal surface area of only 32.8% compared to $MS_6$: Fig 1.7 b). The reason for the accumulation of surface area in the smallest pores is twofold: first, due to the generator there are increasingly more voids of smaller dimension; secondly, the successive coring operations remove most of the surface of the larger pores.

The distribution of pore volumes, on the other hand, differs in the two prefractals: Fig 1.8 b). The Menger-Sponge can accommodate much more adsorbed molecules in its smallest pores $k = 1$. For $n = 6$ the latter give about 7% of the total pore volume compared to only 1.7% in the Menger-Filter of the same generation. The same percentages in the largest pores amount to 31% for $MS_6$ and 49% for $MF_6$.

These differences in geometrical properties of the two porous structures will have important consequences on their adsorption isotherms, as seen in Chapter 4.
1.3.4 Properties related to pore topology

1.3.4.1 Motivation for introducing the concept of cohesion boundary

The current characterization of pore topology in porous media is mainly qualitative [29],
being limited to Euclidean geometries. In this respect the two structures may provide useful
insights:

1. For the Menger-Sponge the set of pores of the same generation is a connected set in
   the sense of set theory, i.e. there is always a path between any two such pores, which
does not cross any other pore generation;

2. In contrast, in the Menger-Filter, pores of the same generation form a non-connected
   set, i.e. every connecting path needs to cross either larger or smaller pores.

In the following, a quantitative measure for the characterization of these properties is
proposed.

1.3.4.2 Cohesion boundary and related quantities

The cohesion boundary between two pore generations: both the Sponge and the Filter
share the property that for each \( i \) and \( j \) with \( 1 \leq i < j \leq n \) (\( n \geq 2 \) ) there exist pores of
generations \( i \) and \( j \), which are adjacent. The cohesion boundary is defined as the sum of
cross-section areas of the holes, through which pores of the given generations \( i \) and \( j \) can
link by cohesion. Formulas for the cohesion boundary \( A_{n,i,j} \) are given in Appendix I, where
the first index \( i \) is always smaller than \( j \). The present definition relies on the following four
assumptions:

A1: the totality of the pores of generation \( k \) is given unequivocally by the \( (n-k+1)^{th} \)
   step of the prefractal generating procedure;

A2: the holes, through which any two pore generations can link by cohesion, are defined
   unequivocally;

A3: the pore size \( l_k \) of the pores of generation \( k \) is taken to be equal to the edge length of
   the cubes removed the \( (n-k+1)^{th} \) step, i.e. \( l_k = 3^{k-1} \cdot l_1 = L / 3^{n-1-k} \), where \( l_1 \) and \( L \)
are the size of the smallest pores and that of the prefractal respectively;
A4: when comparing the Menger-Sponge with the Filter, the size $l_1$ of the smallest pores is assumed to be equal in the two structures. Therefore, the cohesion boundary is restricted to regular prefractals as the ones treated in this thesis.

The total cohesion boundary $A_n$ can be found by summing up the $A_{n,i,j}$'s over all pairs of pore generations $i, j$, where $1 \leq i < j \leq n$, i.e.:

$$A_n = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} A_{n,i,j} \tag{1.4}$$

The contribution from different pairs of pore generations to $A_n$ is determined also by the pore size distribution.

The structure parameter $\Delta_{n,k}$ characterizes the cohesion boundary independently of pore size distribution for each pore generation $k = 1 \ldots n - 1$, and is defined as follows:

$$\Delta_{n,k} = \frac{A_{n,k} \cdot l_k}{V_{n,k}} \tag{1.5}$$

where:

1. $V_{n,k}$ is the pore volume of the $k^{th}$ pore generation;
2. $A_{n,k}$ is the sum of cohesion boundaries of the $k^{th}$ pore generation to the larger pore generations $k + 1$ to $n$, i.e.:

$$A_{n,k} = \sum_{j=k+1}^{n} A_{n,k,j} \tag{1.6}$$

This definition is motivated by the fact that the Menger Sponge allows for adsorption in a strictly porewise manner starting with the smallest pores (see Chapter 4, Fig 4.1)

3. $l_k$ stays for the size of the $k^{th}$ pore generation, i.e. $l_k = 3^{k-1} \cdot l_1$, where $l_1$ is the size of the smallest pores; its role is to make the structure parameter dimensionless.

The assumptions A1-A4 given above make sure that the structure parameter $\Delta_{n,k}$ is well defined.
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In addition, the structure parameter has the following useful properties:

1. it is invariant under scaling transformations of the porous structure;
2. it is invariant under "additive transformations" in the sense that the parameter $\Delta_{n,k}$ of a structure $G$ is the same as that of a structure composed of two $G$'s;

1.3.4.3 Properties of the cohesion boundary in the Sponge and the Filter

The exact formulas comprised in Appendix I allow for a comparison of the various quantities for the two structures, as described below:

**Total cohesion boundary** $A_n$: the variation of the ratio $A_{n,MF} / A_{n,SS}$, as reproduced in Fig 1.9, allows for a comparison of the total cohesion boundaries in the two structures:

- in the range $2 \leq n \leq 4$ the total cohesion boundary of the Menger-Filter exceeds with more than four times that of the Sponge; this illustrates the fact that the set of pores of the same generation in the Menger-Filter is not connected for all $k = 1 \ldots n$ and this can only be achieved through a higher cohesion boundary;
- with $n \geq 10$ the ratio $A_{n,MF} / A_{n,SS}$ drops below 1 and converges to zero as $n \to \infty$; the apparent dominance of the Menger-Sponge in the range $n \geq 10$, however, is due to the higher relative volume of the smaller pores in the Sponge, as shown in Fig 1.8 b);
- to achieve a better correspondence with the mentioned properties of pore structure, the cohesion boundary must be normalized to the volume of the pores.

![Fig 1.9 The ratio of the total cohesion boundaries as function of the parameter $n$](image)
The structure parameter $\Delta_{n,k}$: based on the formulas given in Appendix I, one can study the behavior of the structure parameter $\Delta_{n,k}$ in the two structures as well as its dependence on the parameters $n$ and $k$.

**Fig 1.10** a) The structure parameter of the two structures for $n = 6, 10$; b) variation of the ratio $\Delta_{n,k}^{MF}/\Delta_{n,k}^{MS}$ with $k$ for $n = 6, 10$.

The results shown in Fig 1.10 can be summarized as follows:

1. Influence of prefractal generation $n$: Fig 1.10 a):
   - The structure parameter $\Delta_{n,k}$ shows a rather low sensitivity on the prefractal generation; in particular for $k << n$ (i.e. for the smallest pores) the changes with $n$ are small;

2. Influence of pore generation $k$: Fig 1.10 a):
   - The pore generation $k$ has similarly a rather low influence on $\Delta_{n,k}$; in particular, for large $n$ the structure parameter shows almost no variation with $k$, in agreement with the self-similarity property; larger differences can only be observed when $k$ is closer to $n$, and this is due to the finite range of self-similarity.

3. Differences between the Sponge and Filter: Fig 1.10 b):
   - The variation of the ratio $\Delta_{n,k}^{MF}/\Delta_{n,k}^{MS}$ shows that the cohesion boundary per unit volume in the smallest pores is about seven times larger in the Filter than in the Sponge, while for the other pore generations this ratio lies between 6.47 and 7. Similarly the ratio shows a low sensitivity with respect to $n$ and $k$. 
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1.3.5 Properties of the discretized prefractals

1.3.5.1 Discretization of the prefractals

The discretization consists in embedding the prefractals into a 3D simple cubic lattice of lattice constant \( d \), where \( d = 0.3 \text{nm} \) is the diameter of the model spherical water molecule. This embedding has several implications:

1. \( l_i \geq d \), i.e. the smallest pores must be accessible for water molecules;
2. the ratio \( l_i / d \) must be an integer, i.e. the pore widths of the prefractals must be commensurate with the diameter of the water molecule (incommensurability effects have been treated in [30]);
3. the adsorbed water molecules are restricted to the vertices of the simple cubic lattice.

The ratio \( l_i / d \) gives the width of the smallest pores in units of molecular diameters and will be denoted by \( m \). Each pair of values \( m \) and \( n \) defines a porous body, which will be denoted by \( MS_n(m) \) and \( MF_n(m) \) respectively. The simple cubic arrangement and the fact that \( m \) is an integer give a simple tool for the calculation of various groups of adsorbed molecules, see Appendices I and II. The total pore volume \( V_n \), when expressed in units of \( d^3 \) gives the number \( N_n^{AD} \) of adsorbed molecules at saturation. In a similar way the internal surface \( S_n \), expressed in units of \( d^2 \) gives the number of molecules needed to cover an open flat surface of the same area.

1.3.5.2 Implications of the confined pores after discretization

The main implication of the confined pores is a qualitative difference compared to the adsorption on an open flat surface. In the following, the geometric characteristics of this difference are analyzed in the discretized case.

Adsorption sites with different binding energies: in a first approximation, it is assumed that the porous solid interacts with molecules adsorbed in the first layer only. As a result, the binding energy of an adsorbed molecule is determined by the number of adjacent adsorbent molecules: Fig 1.11. a). In the two self-similar structures five types of adsorption sites can be found, and these will be referred to as the five adhesion types:
- 4a: only in the smallest pores of width equal to the diameter of the water molecule, i.e. only for \( m = 1 \) and \( k = 1 \);
- 3a: or corner molecules do not appear in MS but occur in the MF and may occur in real structures;
- 2a: molecules on the edges of the pores at least two molecular diameters wide;
- 1a: molecules on the planes of the pores at least three molecular diameters wide;
- 0a: molecules in upper layers, if one neglects interactions over more than one layer.

The number of each adhesion type in the two structures can be calculated exactly and these are given in Appendix II.

**Fig 1.11** a) Adhesion types in the Menger-Sponge \((m = 1)\); b) Distribution of the adhesion types for \( MS_4(m = 1) \) and \( MF_4(m = 1) \) compared to the total adsorbed amount respectively.

**Distribution of adhesion types in the two structures:** the distribution of adhesion types for \( MS_4(m = 1) \) and \( MF_4(m = 1) \), given in percentages compared the amount of molecules at saturation, is given in Fig 1.11b). The relative amount of adsorption sites of energy 4a is almost twice as large for the \( MS_4(m = 1) \) as for the \( MF_4(m = 1) \). In the same time, in the \( MF_4(m = 1) \) the relative amount of adsorption sites of type 0a exceeds the corresponding value for the \( MS_4(m = 1) \) with almost 20%. The dominance of surface effects for the \( MS_4(m = 1) \) can also be seen from the percentages of adhesion types 2a and 1a. The sum of sites with at least one solid neighbor gives 36.1% compared to only 17.4 % for \( MF_4(m = 1) \).
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Fig 1.12 shows the dependence of the distribution of adhesion types on the parameter $m$ for the third generation Menger-Sponge. The sites of highest adsorption energy $4a$ are present only in the smallest pores and for $m = 1$, while the relative amount of the types $0a$ increases monotonically with $m$. In the same time, the percentages of adsorption sites with at least one solid neighbor decrease, assuming the values 52.4%, 40.1%, 32% and 26% respectively. One can also observe a difference in the distributions when $m \leq 2$ and $m \geq 3$: while in the former case the percentages have a minimum at $2a$ and $1a$ respectively, for $m \geq 3$ they form a strictly increasing sequence.

![Graph](image1.png)

**Fig 1.12** Distribution of adhesion types for $MS_3$ as a function of $m = 1...4$

Comparing the values for $MS_3(m = 1)$ on Fig 1.12 with those of $MS_4(m = 1)$ on Fig 1.11 b) reveals also how the distributions depend on the prefrcial generation $n$. Similarly to the dependence on $m$, the volume effects become dominant if $n$ is increased. The dependence on $n$ and $m$ in the case of the Menger-Filter is quite similar to the Sponge, as revealed on Figs 1.11 b) and 1.13. Differences can be observed in the presence of the
adhesion type 3α and in the dominance of the type 0α, in agreement with the higher porosity of the Menger-Filter.

**Differences compared to an open flat surface:** the difference between adsorption on an open flat surface and on exact fractal models of nanoporous materials is illustrated on Fig. 1.14, showing a vertical section of a flat surface and that of a small pore.

![Fig 1.14 Vertical sections of an open flat surface and of a pore; the darkest molecules define the monolayer coverage and coloring indicates the successively adsorbed layers](image)

![N[%, r [%](1) vs. layers](image)

![r [%] vs. m](image)

**Fig 1.15** a) Cumulative number of molecules in consecutive layers normalized to the number of molecules at saturation; b) percentage \( r \) of the estimated to the real surface area as a function of \( m \); the estimated surface area is defined as the product of the number \( N_{\text{mono}} \) of molecules, needed to build a monolayer, with the surface area \( d^2 \) occupied by a single molecule.

The differences can be summarized as follows:

1. the layers of higher order have a smaller extension than the layers of lower order. The cumulative number of molecules in consecutively adsorbed layers for the Sponge and
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the Filter, shown in Fig 1.14 a), deviates considerably from the simple linear dependence characteristic for a plane surface.

2. For a flat surface the product of the number of molecules needed to build a monolayer multiplied by the area $d^2$ occupied by a single molecule is simply the area of the surface. For a porous medium, on the other hand, this results in an underestimation of surface area: Fig 1.14 b), since molecules in the monolayer may touch several walls. The underestimation is considerable, between 40–80%, especially for small pores.
Chapter 2 The lattice-gas description of adsorption

2.1 The lattice-gas model (LG)

2.1.1 Description in the Grand Canonical Ensemble

The LG is the simplest model in statistical mechanics that exhibits a first order phase-transition (provided its dimensionality is higher than one). It is equivalent to the Ising model of ferromagnets and to several other models describing phase-transitions in a variety of physical systems. The name “Lattice-Gas” has been coined by Lee and Yang [31, 32] who first showed that it provides a qualitatively reliable model of a condensing gas.

The LG is defined as follows. Consider e.g. a simple cubic lattice of \( N_{\text{sat}} \) (saturation number) vertices and a collection of \( 0 \leq N \leq N_{\text{sat}} \) particles. The particles are placed on the vertices of the lattice such that no more than one particle can occupy a given lattice site and only nearest neighbor particles interact. The potential energy of interaction of two particles \( i \) and \( j \) is therefore:

\[
U_{ij} = \begin{cases} 
  +\infty & \text{if } i = j \\
  -c & \text{if } i \text{ and } j \text{ occupy neighboring sites } (c > 0, \text{attraction}) \\
  0 & \text{otherwise}
\end{cases}
\]  

(2.1)

The kinetic energy of the particles is neglected.

If one introduces the parameters \( n_i \) for each lattice site \( i \) such that:

\[
n_i = \begin{cases} 
  1 & \text{if site } i \text{ is occupied} \\
  0 & \text{if site } i \text{ is unoccupied}
\end{cases}
\]

(2.2)

then, the number \( N \) of particles and the total potential energy \( E \) of a configuration \( \{ n_i \} \) are given by

\[
N\{n_i\} = \sum_i n_i \quad \text{and} \quad E\{n_i\} = -c \sum_{(ij)} n_i n_j 
\]

(2.3a,b)

respectively, where the second sum runs over all nearest neighbor sites \( i \) and \( j \). The grand canonical partition function \( Q_G \) of the LG is given by
where $\mu$ is the chemical potential, $\gamma$ denotes the dimensionless fugacity, and $Z_N$ is the canonical partition function of an $N$-particle subsystem,

$$Z_N = \sum_{N=0}^{N_{\text{sat}}} e^{-\frac{\mathcal{H}[\eta]}{kT}}$$ \hfill (2.5)

The pressure $p$ and the average number of particles $\langle N \rangle$ result from $Q_G$ as follows

$$p = \frac{kT}{N_{\text{sat}}} \cdot \ln Q_G, \quad \langle N \rangle = kT \frac{\partial \ln Q_G}{\partial \mu} = \gamma \frac{\partial \ln Q_G}{\partial \gamma}, \quad \hfill (2.6a,b)$$

The density $\rho = \langle N \rangle / N_{\text{sat}}$ is obtained as

$$\rho = \gamma \frac{\partial \ln Q_G}{\partial \gamma} = \gamma \frac{\partial}{\partial \gamma} \left( \frac{p}{kT} \right) \hfill (2.7)$$

Equations (2.6a) and (2.7) represent the equation of state of the LG in a parametric form, the parameter being the fugacity. This parameter can in general not be eliminated analytically from Eqs. (2.6a) and (2.7), except for the low density limit $\rho \ll 1$. Indeed, in the latter case the canonical partition function $Z_N$ can be approximated with the number of possible arrangements of $N$ particles over $N_{\text{sat}}$ lattice sites, such that:

$$Q_G = \sum_{N=0}^{N_{\text{sat}}} \gamma^N \cdot \frac{N_{\text{sat}}!}{N! (N_{\text{sat}} - N)!} = (1 + \gamma)^{N_{\text{sat}}} \hfill (2.8)$$

Substituting Eq. (2.8) into Eqs. (2.6a) and (2.7), one obtains

$$p = kT \cdot \ln (1 + \gamma) \quad \text{and} \quad \rho = \gamma / (1 + \gamma) \hfill (2.9a,b)$$

respectively. In this way we get

$$p = kT \cdot \ln \left( \frac{1}{1 - \rho} \right) \approx kT \rho \quad \text{for} \quad \rho \ll 1 \hfill (2.10)$$
Therefore, one recovers the equation of state of the ideal gas as the low density limit of the LG. Equation (2.9a) also shows that for small values of the fugacity (where \( \ln(1 + \gamma) \approx \gamma \) holds) the pressure is proportional (at any given temperature) to its fugacity,

\[
p = kT\gamma \quad \text{(for } \gamma \ll 1) \quad (2.11)
\]

2.1.2 The phase-transition

In spite of its restrictive basic assumptions (neglected kinetic energy, particles restricted to a lattice), the LG model reproduces the main features of a real gas, namely, as shown already by Lee and Yang [31, 32], it predicts the existence

(i) of a critical temperature \( T_c \) (in more than one dimension), and

(ii) of a phase transition of first kind to a condensed state at every \( T < T_c \).

This analogy is illustrated in Fig. 2.1, where the experimental and the LG-model compression isotherms \( \rho = \rho(p, T = \text{const.}) \) of a real gas are shown.

![Fig 2.1](image)

**Fig 2.1** Compression isotherms \( \rho = \rho(p, T = \text{const.}) \) of a real gas as obtained experimentally (a) and from its present LG model (b).

The LG-model isotherms can be obtained from the parametric expressions of the density \( \rho \) and the pressure \( p \) in terms of the fugacity \( \gamma \), as deduced from the partition function \( Q_G \) according to Eqs. (2.4), (2.6a) and (2.7). This procedure emphasizes the following features of the LG-description:
1. For small values of $\rho$, according to Eqs.(2.11) and (2.9b), both $\rho$ and $p$ increase linearly with $\gamma$, such that for $p$ and $\rho$ the linear relationship (2.10) holds. In this way, in the corresponding linear parts of the LG-isotherms (b), one recovers the ideal gas behavior, in full agreement with the shape of the experimental isotherms (a). This behavior holds both for $T \leq T_c$ and $T \geq T_c$.

2. For any given value of temperature in the range $T < T_c$, both $p$ and $\rho$ remain smooth monotonic increasing functions of the increasing fugacity until a certain value:

$$\gamma = \gamma_0 = e^{\frac{z\varepsilon}{2kT}} = e^{\frac{3\varepsilon}{kT}}$$  \hspace{1cm} (2.12)

determined by the coordination number $z = 6$ of the simple cubic lattice. At this value of the pressure the density undergoes a discontinuity of the first kind, i.e. the function $\rho(\gamma)$ may take for $\gamma = \gamma_0$ any value between a lower and an upper bound, $\underline{\rho}(\gamma_0) \leq \rho(\gamma_0) \leq \bar{\rho}(\gamma_0)$ where $\bar{\rho}(\gamma_0) = 1 - \underline{\rho}(\gamma_0)$ (see Fig. 2.1b). In this density range the liquid phase coexists with the saturated vapor phase of the LG. The upper limit $\bar{\rho}(\gamma_0)$ represents obviously the density of the liquid phase, while the lower limit $\underline{\rho}(\gamma_0)$ is associated with the maximum density of the saturated vapor phase of the lattice gas (at the specified temperature). Therefore, any value in the range $\underline{\rho}(\gamma_0) \leq \rho(\gamma_0) \leq \bar{\rho}(\gamma_0)$ corresponds to the different proportions of liquid and saturated vapor phases.

3. According to Eq. (2.7), the derivative of the pressure $p$ with respect to $\gamma$ also becomes singular at $\gamma = \gamma_0$.

4. As the temperature increases towards the critical value $T_c$, the coexistence range $[\underbar{\rho}(\gamma_0), \overline{\rho}(\gamma_0)]$ becomes narrower and shrinks to a point when $T$ reaches the value $T_c$. The envelope of the points $\rho(\gamma_0)$ and $\bar{\rho}(\gamma_0)$ obtained for all values $T \leq T_c$ specifies the whole coexistence domain in the phase plane $(p, \rho)$.

5. The critical temperature of the LG depends only on the potential energy $c$ of the nearest-neighbor interaction and the type of the lattice considered. For the simple cubic lattice one has [33]:

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1. For small values of $\rho$, according to Eqs.(2.11) and (2.9b), both $\rho$ and $p$ increase linearly with $\gamma$, such that for $p$ and $\rho$ the linear relationship (2.10) holds. In this way, in the corresponding linear parts of the LG-isotherms (b), one recovers the ideal gas behavior, in full agreement with the shape of the experimental isotherms (a). This behavior holds both for $T \leq T_c$ and $T \geq T_c$.

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5. The critical temperature of the LG depends only on the potential energy $c$ of the nearest-neighbor interaction and the type of the lattice considered. For the simple cubic lattice one has [33]:
\[
\frac{c}{kT_c} = 0.8866 \quad \text{i.e.} \quad kT_c = 1.1279c
\] (2.13)

6. The phase transition in the lattice-gas model allows also for the definition of the relative fugacity \( \gamma_{rel} \):

\[
\gamma_{rel} = \gamma / \gamma_0 = e^{(\mu - \mu_0)/kT} = e^{(\mu + 3c)/kT},
\] (2.14)

The relation to the relative pressure is given in the next section 2.1.3.

One of the limitations of the LG model, illustrated also on Fig 2.1, is that it does not obey the "law of rectilinear diameter" [34]. This law states that the sum of the vapor and liquid densities in equilibrium increases linearly with decreasing temperature and explains the asymmetric shape of the coexistence curve of a real gas Fig 2.1 a). On the other hand, the coexistence curve of the LG is symmetric to the line of the critical density \( \rho_c = 0.5 \), such that the relation \( \rho(\gamma_0) + \rho(\gamma_0) = 2\rho_c = 1 \) holds for all \( T \leq T_c \).

Nevertheless, the lattice-gas model shows the main qualitative aspects of a phase transition. Therefore, it can be considered both as a first approximation to a real gas as well as the basis for a more general adsorption model.

2.1.3 Justification for the linear dependence of pressure versus fugacity

The density of the 3D lattice-gas (Eq. 2.6) is an ensemble average, therefore it can easily be estimated using Grand Canonical Monte Carlo simulation. The pressure, on the other hand, which is needed later for the representation of adsorption isotherms (section 2.2) is much more difficult to determine [35] and one must rely on approximations.

A possible approximation is suggested by the behavior of the water vapor itself. There is experimental evidence that, under certain conditions, water vapor can be approximated by an ideal gas:

1. below \( T = 400 \, K \) the vapor-liquid phase boundary can very well be fitted by the Clausius-Clapeyron equation [36]; however, this equation is deduced assuming the gas phase to be ideal;
2. below \( T = 400 \, K \) the deviation from the linear dependence between the fugacity and the pressure of the water vapor is very small [37]; at \( T = 300 \, K \) this difference amounts to only 0.1%.
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The same property, i.e. the linear dependence between the pressure and the dimensionless fugacity, has been proven to hold for the LG (see Eq. (2.11)) provided $\rho \ll 1$. Whether this approximation can be extended up to saturation:

$$p \approx kT\gamma \quad \text{for all } \gamma \leq \gamma_0$$  \hspace{1cm} (2.15)

must however be ascertained for this model. Relying on earlier results obtained for the Ising model, it can be shown that the approximation (2.15) is valid, provided one is well below the critical temperature:

a) The equation of state of 2D lattice-gas (based on its equivalence with the 2D Ising model) can be given in a closed form at the saturation pressure [38]. Therefore, the dependence of pressure on the dimensionless fugacity is exactly known at $\gamma = \gamma_0$, see [32]. Using this relation, the ratio $r = p_0 / kT\gamma_0$ can be plotted as a function of the reduced cohesion. Fig. 2.2 shows that below a temperature of about $T = T_{\text{crit}}/2$ the approximation (2.15) is acceptable. Although this result applies only for the 2D case, it suggests that one might have a similar situation in the 3D case, too.

![Fig. 2.2 Results for the 2D lattice-gas model](image)

b) The above approach unfortunately does not work in the 3D case. However, approximate results for the magnetization in the 3D Ising model in zero magnetic field are available in the literature. Reference [39] presents results obtained by Wolff Cluster simulation yielding accurate values for the magnetization in the range $0.0005 < t < 0.26$, with $t = (T_{\text{crit}} - T) / T_{\text{crit}}$, i.e. at temperature below but close to the critical point. Another work [40] gives low temperature series expansions of the magnetization using direct enumeration of so-called
relevant configurations. Based on the equivalence between the LG and the Ising model, these results can be formulated in terms of the lattice gas. The densities $\rho(\gamma_0)$ and $\overline{\rho}(\gamma_0)$ at the coexistence curve versus the reduced cohesion (Fig 2.3) can be obtained by using the relation:

$$\rho = \frac{m+1}{2}$$

(2.16)

which links the density $\rho$ and the magnetization $m$ in the two models, see for instance [41].

![Graph showing approximations to the coexistence curve at two different resolutions](image)

**Fig 2.3** Approximations to the coexistence curve at two different resolutions

There is a wide temperature range below the critical temperature where the two methods lead to similar results. Moreover, at $c/kT = 2$ (corresponding to water vapor at room temperature, as shown in section 2.3) the density of the gas phase at the saturation point is only about $\rho(\gamma_0) = 0.003$, being smaller for more than two orders of magnitude than the critical density $\rho_c = 0.5$. From here the validity of Eq. (2.15) does not follow directly, one can be sure, however, that at densities less than $\rho = 0.003$ this approximation is not very far from reality. Combining Eq. (2.14) with the approximation (2.15) allows for the definition of the relative pressure in terms of:

$$\lambda = \frac{p}{p_0} = \frac{\gamma}{\gamma_0} = e^{(\mu-\mu_0)/kT}$$

(2.17)

Adsorption isotherms in the following chapters are going to be represented according to this definition.
2.2 Lattice-gas description of adsorption of a real gas in 3D prefractals

The adsorption model is constructed by embedding the prefractal structures into the already defined 3D lattice. The geometric description of this embedding has been given in section 1.3.5, here only the thermodynamics of the system is discussed.

Any vertex of the adsorption model may either be unoccupied, or occupied by an adsorbed water molecule or by a molecule of the self-similar solid, respectively. In principle this may result in three types of interactions:

1. **water-water interactions**: nearest neighbor water molecules are assumed to interact through a cohesion energy \(-c\), i.e. through the potential given in Eq. (2.1)
2. **water-solid interactions**: nearest neighbor molecules of the two components interact through an adhesion energy \(-a\);
3. **solid-solid interactions**: the solid adsorbent is assumed to be inert, i.e. the state of the solid is not influenced by adsorption. Therefore, its energy can be considered as the zero energy of the adsorption model.

Based on these assumptions and the notation introduced in Eq. (2.2), the interaction energy of a given configuration \(\{n\}\) determined by an arrangement of \(N = \sum_i n_i\) adsorbed molecules is given by:

\[
E\{n\} = -c \sum_{(ij)} n_i n_j - a \sum_i^{*} \text{adh}_i \cdot n_i
\]  

(2.18)

where the starred sum is over sites that are nearest neighbors to at least one solid molecule and \(\text{adh}_i\) gives the number of nearest neighbor solid particles to the adsorption site \(i\).
In the above adsorption model the gas which fills the surroundings of the porous structure is explicitly not included (Fig. 2.4 b). Indeed, under the assumption that surface effects at the interface between the gas and the external boundary of the porous structure can be neglected, the simplification suggested in Fig 2.4 b) over Fig 2.4.a) is legitimate. The only condition imposed on the system is that of thermodynamic equilibrium with a reservoir, the considered states belonging to the Grand Canonical Ensemble.

\[ p = \frac{kT}{N_{sat}} \ln Q_G(\mu) \quad \text{and} \quad \theta = \frac{kT}{N_{AD}^{sat}} \frac{\partial \ln Q_{AD}(\mu)}{\partial \mu}, \tag{2.19a,b} \]

respectively. The isotherms are obtained from the above relations by keeping in mind that at thermodynamic equilibrium the condition \( \mu_{AD} = \mu_G \) holds for the two systems:

\[ \theta = \frac{\gamma}{N_{sat}^{AD} Q_{AD}(\gamma)} \frac{\partial Q_{AD}(\gamma)}{\partial \gamma} = \frac{\sum_{N=1}^{N_{AD}} \bar{N} \cdot Z_N^{AD} \cdot y^{-3N} \gamma_N^{YM}}{N_{sat}^{AD} \left( 1 + \sum_{N=1}^{N_{AD}} Z_N^{AD} \cdot y^{-3N} \gamma_N^{YM} \right)} \tag{2.20} \]
where $\gamma_{\text{rel}}$ is the relative fugacity defined in Eq. 2.14 and

$$y = \gamma_0^{-1/3} = e^{\gamma/kT} \quad (2.21)$$

Under the condition that the approximation (2.17) for the relative pressure is valid, one has:

$$\theta = \frac{\sum_{N=1}^{N_{\text{sat}}} N \cdot Z_N^{AD} \cdot y^{-3N} \lambda^N}{N_{\text{sat}} \cdot \left(1 + \sum_{N=1}^{N_{\text{sat}}} Z_N^{AD} \cdot y^{-3N} \lambda^N\right)} \quad (2.22)$$

Beside the so-called total isotherm given in Eq. (2.22) above, the adsorption to certain subcategories of adsorption sites can also be studied (see Chapters 3 and 4). The group of molecules, which adsorb to these sites, will be called a population, while the isotherm of that population will be called its partial isotherm. According to the applied normalizing constant, it will be distinguished between the relative:

$$\theta_{\text{rel}}^\text{pop} = \frac{\langle N^\text{pop} \rangle}{N_{\text{sat}}} \quad (2.23)$$

and the absolute partial isotherm:

$$\theta_{\text{abs}}^\text{pop} = \frac{\langle N^\text{pop} \rangle}{N_{\text{sat}}} \quad (2.24)$$

where $N_{\text{sat}}^\text{pop}$ denotes the total number of adsorption sites of a certain category, while $\langle N^\text{pop} \rangle$ stays for the average number of occupied adsorption sites of that category, according to the distribution determined by the grand canonical partition function.

Adsorption isotherms in the following chapters will either be obtained by the exact calculation of the canonical partition functions $Z_N^{AD}$ or by Grand Canonical Monte Carlo simulations. These methods will be used for small and large systems in Chapters 3 and 4 respectively.
2.3 Determination of simulation parameters for the case of water vapor

2.3.1 Estimation of the cohesion energy

The existence of a first-order phase-transition in the 3D lattice-gas model provides a simple method for the estimation of the cohesion energy \( c \) in the case of water vapor. Having in mind Eq. (2.13) and knowing that the critical temperature of the water vapor is \( T_c = 647 \, K \), it follows that:

\[
c = 0.8866 \cdot k \cdot T_c = 0.8866 \cdot 1.38 \cdot 10^{-23} \cdot 647 \, J = 7.92 \cdot 10^{-21} \, J
\]  

(2.25)

The reduced cohesion \( c/kT \) can be expressed as:

\[
\frac{c}{kT} = \frac{c}{kT_c} \cdot \frac{kT_c}{kT} = \frac{0.8866 \cdot 647}{T} = \frac{573.63}{T}
\]  

(2.26)

<table>
<thead>
<tr>
<th>Property/Model/Source</th>
<th>Method/Field</th>
<th>cohesion energy ( c , [10^{-21} , J] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latent heat of condensation</td>
<td>sum of nearest neighbor interactions</td>
<td>( 11.24 \leq c \leq 33.74 )</td>
</tr>
<tr>
<td>Surface tension [42]</td>
<td>break pair interactions to build a surface</td>
<td>( c = 19.84 )</td>
</tr>
<tr>
<td>Critical temperature [33, 43]</td>
<td>Lattice-Gas model</td>
<td>( c = 7.92 )</td>
</tr>
<tr>
<td>Rowlinson model [44]</td>
<td>Molecular Dynamics</td>
<td>( c = 37.55 )</td>
</tr>
<tr>
<td>ST2 model [44]</td>
<td>Molecular Dynamics</td>
<td>( c = 47.5 )</td>
</tr>
<tr>
<td>Pauling [46]</td>
<td>Quantum Mechanics</td>
<td>( c = 31.27 )</td>
</tr>
<tr>
<td>Lennard-Jones et al [47]</td>
<td>Quantum Mechanics</td>
<td>( 25.08 \leq c \leq 39.95 )</td>
</tr>
<tr>
<td>Chakravorty et al [48]</td>
<td>Microwave Spectrum</td>
<td>( c = 37.52 )</td>
</tr>
</tbody>
</table>

Table 2.1 The cohesion energies \( c \) for water as determined by various methods

Choosing the temperature range relevant for building materials (\( T_{\text{min}} = -20^\circ C \) or \( 253K \) to \( T_{\text{max}} = 40^\circ C \) or \( 313K \)), one obtains for the reduced cohesion:

\[
1.83 \leq \frac{c}{kT} \leq 2.3
\]  

(2.27)
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In this thesis the value of $c/kT = 2$ is used mostly for the calculation of adsorption isotherms. According to Eq. (2.26) this value corresponds to $T = 286.8 \, K$ or 13.8°C.

The cohesion energies $c$ for water, as determined by other methods (Table 2.1) are larger, though of the same order of magnitude. The reason for this difference is that the cohesion energy $c$ as calculated in Eq. (2.25) is the correct value for a LG, which mimics water vapor, but not the real effective interaction between two water molecules. Moreover, in the range under study ($c/kT \approx 2$), the linear approximation to the relative pressure (Eq. 2.17) is valid, as shown in section 2.1.3.

### 2.3.2 Estimation of the adhesion energy

In the previous subsection the cohesion energy $c$ (Eq. (2.25)) was chosen such as to be in accordance with the lattice-gas model. Its value being thus fixed, the adhesion energy can be expressed by means of the adhesion to cohesion ratio $a/c$. For the latter quantity the range:

$$0 \leq a/c \leq 3$$

is reasonable. The lower limit results from the restriction to attractive adhesion forces (exothermal adsorption). No qualitative changes occur in the isotherms above $a/c = 3$, as shown in the next chapters.

<table>
<thead>
<tr>
<th>Method</th>
<th>Source</th>
<th>adsorption energy per molecule [10^{-21}J]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring the heat of adsorption of water on cement</td>
<td>Powers and Brownyard [50]</td>
<td>107.47...111.24</td>
</tr>
<tr>
<td></td>
<td>Brouwers [51]</td>
<td></td>
</tr>
<tr>
<td>Using the parameter $c_{BET}$ of the BET theory obtained by curve fitting</td>
<td>Powers and Brownyard [50]</td>
<td>79.14...80.43</td>
</tr>
<tr>
<td></td>
<td>Setzer [52]</td>
<td>76.99...78.53</td>
</tr>
<tr>
<td></td>
<td>Hagymassy et al [53]</td>
<td>78.93...86.80</td>
</tr>
<tr>
<td></td>
<td>Niklasson [6]</td>
<td>80.43</td>
</tr>
</tbody>
</table>

**Table 2.2** Adsorption energy per water molecule in the first adsorbed layer using adsorption measurements.
In this context values of the adhesion energy derived from macroscopic measurements of the water-cement system must be considered only as informative: Table 2.2. These values are several times higher than it would be expected from the lattice gas model. However, it must be noted that these results are derived from the microscopic interpretation of macroscopic measurements.
Chapter 3 Exact results for the small systems

For the case of the small systems $MS_i(m)$ and $MF_i(m)$ with $m = 1, 2$ (Fig 3.1) the partition functions $Q_{\text{AD}}$ and thus the isotherms $\theta = \theta(\gamma_{\text{rel}})$ can be calculated exactly, as described in Appendix III. Therefore, the dependence on temperature and adhesion to cohesion ratio can accurately be determined.

Over the parameter range where the linear approximation (2.17) is valid ($c/kT \geq 2$, $\lambda \leq 1$), these isotherms can simply be expressed as $\theta = \theta(\lambda)$ and all results can be represented in terms of the relative pressure.

In order to fully explore the possibilities of the exact approach, however, the analysis is extended over a wider range of parameters (e.g. $T > T_c$ or $\lambda > 1$), i.e. also were the linear relationship (2.17) may not be accurate. In these cases the analysis is limited to qualitative statements.
3.1 Description of the small systems

The small systems, being first generation prefractals, do not show any self-similarity and possess a fairly simple pore structure. Such systems are frequently used as models of molecular sieves [18, 19]. The unit cells of zeolites of type A, X and Y, built up from $SiO_4$ and $AlO_4$ tetrahedra joined through oxygen atoms [54], are in fact identical to the first generation Menger-Sponge. They have pores of molecular dimensions $0.3 - 0.8 \text{ nm}$, into which guest molecules can penetrate. The cases $m=1,2$ for the two prefractals correspond exactly to this range of pore diameters.

![Fig 3.1 First generation prefractals](image)

Properties, which are relevant for adsorption, can easily be recognized on these structures:

- the presence of adsorption sites with binding energies $0a$ up to $4a$ due to the proximity of several “walls” (energetic heterogeneity of geometric origin);
- the mean number $N_{a,sat}^{AD} / N_{sat}^{AD}$ of adhesion contacts per molecule at saturation, which gives a measure of the importance of adsorbent surface in confined spaces;
- the mean number $N_{c,sat}^{AD} / N_{sat}^{AD}$ of cohesion contacts per molecule, expressing the steric constraints imposed by the confined spaces on the coordination number of the adsorbate; it determines the ability of the structure to promote the building of aggregates of adsorbed molecules;
- the size $\bar{N}$ of the largest connected cluster of adsorbed molecules at saturation, playing a similar role in promoting the building of aggregates.
Table 3.1 Geometrical characteristics of the four small systems

<table>
<thead>
<tr>
<th>Structure</th>
<th>$N_{sat}^{AD}$</th>
<th>4a</th>
<th>3a</th>
<th>2a</th>
<th>1a</th>
<th>0a</th>
<th>$N_{a,sat}^{AD}/N_{sat}^{AD}$</th>
<th>$N_{c,sat}^{AD}/N_{sat}^{AD}$</th>
<th>$\bar{N}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$MS,(m=1)$</td>
<td>7</td>
<td>6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>3.428</td>
<td>1.285</td>
<td>7</td>
</tr>
<tr>
<td>$MS,(m=2)$</td>
<td>56</td>
<td>—</td>
<td>—</td>
<td>48</td>
<td>—</td>
<td>8</td>
<td>1.714</td>
<td>2.143</td>
<td>56</td>
</tr>
<tr>
<td>$MF,(m=1)$</td>
<td>12</td>
<td>12</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>$MF,(m=2)$</td>
<td>96</td>
<td>—</td>
<td>24</td>
<td>48</td>
<td>24</td>
<td>—</td>
<td>2</td>
<td>2</td>
<td>32</td>
</tr>
</tbody>
</table>

The geometrical parameters given in Table 3.1 show the following features of the four model adsorbents:

- each structure is characterized by a well-defined distribution of adsorption energies: sites of type 4a can only be found for $m=1$, while positions with no solid neighbors (i.e. 0a) occur only in the central pore of the Menger-Sponge;

- the mean number of adhesion contacts per molecule $N_{a,sat}^{AD}/N_{sat}^{AD}$ is higher for the Menger-Filter and decreases with $m$; all values exceed $N_{a,sat}^{AD}/N_{sat}^{AD} = 1$, which corresponds to the monolayer adsorption on an open flat surface;

- conversely, the mean number of cohesion contacts per molecule $N_{c,sat}^{AD}/N_{sat}^{AD}$ is higher for the Menger-Sponge and increases with $m$; in addition it is significantly lower than the value of $N_{c,sat}^{AD}/N_{sat}^{AD} = 3$, which corresponds to the 3D lattice gas;

- the structure of the Menger-Filter at $n=1$ implies that the size $\bar{N}$ of the largest connected cluster at saturation is smaller than the saturation number $N_{sat}^{AD}$; this prevents the building of aggregates, and leads to significant simplifications in the calculations, as explained in the first section of Appendix III.
3.2 Behavior of the isotherms at the limit of the parameters

To test the applicability of the lattice-based adsorption model and to get first insights, its behavior at the limit of the parameters is analyzed in the following cases:

1. the limit of infinite temperature $T \to \infty$ ($c/kT \to 0$, $a/kT \to 0$);
2. the case of zero cohesion ($a/kT = 0$ and $c/kT = 0$);
3. the limit $a/c \gg 1$ at subcritical temperatures;
4. the limit $0 \leq a/c << 1$ at subcritical temperatures;

The analysis can be done without any difficulty for the four small systems, where exact formulas for the isotherms are available. In the first two cases given above, however, the results can also be generalized to arbitrary porous structures, as shown below.

1. Calculation of the isotherm for $T \to \infty$: in order to study the behavior of the isotherm $\theta = \theta(\gamma, T')$ in the limit $T \to \infty$, the canonical and grand canonical partition functions $Z_{AD}^{\text{can}}$ and $Q_{AD}^{\text{GC}}$ are estimated first. For this purpose, one relies on the general equations (2.4)-(2.7), which are valid for every system having a defined energy function. For the canonical partition function each term in the sum of Eq. (2.5) can be made arbitrarily close to 1 (if a high enough temperature is chosen), and therefore $Z_{AD}^{\text{can}}$ can be approximated by the number of possible arrangements of $N$ particles over $N_{\text{sat}}^{\text{AD}}$ lattice sites:

$$Z_{AD}^{\text{can}} \approx \frac{N_{\text{sat}}^{\text{AD}}!}{N! \left(N_{\text{sat}}^{\text{AD}} - N\right)!} \quad \text{for } T \to \infty \quad (3.1)$$

From here the grand canonical partition function (Eq. (2.4a,b)) can be estimated as:

$$Q_{AD}^{\text{GC}} \approx \sum_{N=0}^{N_{\text{sat}}^{\text{AD}}} \gamma^N \frac{N_{\text{sat}}^{\text{AD}}!}{N! \left(N_{\text{sat}}^{\text{AD}} - N\right)!} = (1 + \gamma)^{N_{\text{sat}}^{\text{AD}}} \quad \text{for } T \to \infty \quad (3.2)$$

One may observe the strong similarities between the low-density limit $\rho << 1$ for the 3D lattice gas discussed in section 2.1.1 (Eq. 2.8) and the present study of the $T \to \infty$ limit.
The adsorption isotherm for \( T \rightarrow \infty \) can be calculated by introducing the approximation (3.2) into the expression (2.20):

\[
\theta \approx \frac{\gamma}{N_{sat}^{AD} \cdot (1 + \gamma)^{N_{sat}^{AD}}} \cdot \frac{C(1 + \gamma)^{N_{sat}^{AD}}}{C} = \frac{\gamma}{N_{sat}^{AD} \cdot (1 + \gamma)^{N_{sat}^{AD}}} \cdot (1 + \gamma)^{N_{sat}^{AD} - 1}
\]

(3.3)

which is to be understood as:

\[
\lim_{T \rightarrow \infty} \theta(\gamma, T) = \frac{\gamma}{1 + \gamma}
\]

(3.4)

Since \( \lim_{T \rightarrow \infty} \gamma_0 = \lim_{T \rightarrow \infty} e^{-3c/kT} = 1 \) holds, one can express the isotherm as function of the relative fugacity as follows:

\[
\lim_{T \rightarrow \infty} \theta(\gamma, T) = \frac{\gamma_{rel}}{1 + \gamma_{rel}}
\]

(3.5)

Figure 3.2 demonstrates, for the four small systems, the successive approximation of this limit for increasing temperatures.

**Relation of the limit isotherm to the chemical potential:** Regarding the isotherm as function of the chemical potential \( \mu \), the limit isotherm is given by the horizontal line at \( \theta = 0.5 \), as shown in Fig 3.3 a). The same isotherm, when represented as function of the relative fugacity, however, does not contain any horizontal portions. This is because the horizontal line at \( \theta = 0.5 \) of Fig 3.3 a) is transformed into the point \( (\gamma_{rel} = 1, \theta = 0.5) \) on Fig 3.3 b). On the other hand, according to Eq. 2.14, for \( \gamma_{rel} < 1 \) the chemical potential goes to \( -\infty \) and for \( \gamma_{rel} > 1 \) it goes to \( +\infty \), when \( T \rightarrow \infty \): Fig 3.3 b).
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Fig 3.2 Adsorption isotherms of the four small structures at $c/kT = 1$, 0.4, 0.2 and 0.1 respectively as indicated in the upper left picture. The dashed curves represent the isotherm for $T \to \infty$ (Eq. 3.5), $\alpha/c$ is supposed to be: $\alpha/c = 1$.

Fig 3.3 The limit isotherm as a function of a) the chemical potential (reproduced for $MS_1(m=1)$ with $\alpha/c = 0.5$ and shown with the horizontal dashed line) and b) of the relative pressure and relative fugacity. The arrows in Fig. 3.3 a) point towards the limit of $T \to \infty$, the chemical potential is given in units of $c = 7.92 \cdot 10^{-21} J$ (Eq. 2.25.)
Relation of the isotherm to the relative pressure in the limit: to obtain the limit isotherm as function of the relative pressure one uses Eq. (2.6a):

\[ p = \frac{kT}{N_{sat}} \ln Q_G(\gamma) \quad \text{and} \quad p_0 = \frac{kT}{N_{sat}} \ln Q_G(\gamma_0) \]  

(3.6a,b)

which gives for the relative pressure:

\[ \lambda = \frac{p}{p_0} = \frac{\ln Q_\gamma(\gamma)}{\ln Q_\gamma(\gamma_0)} \]  

(3.7)

For high enough temperatures the pressure \( p \) can be estimated, similarly to the case of small density, according to Eq. 2.9a:

\[ p \approx kT \cdot \ln(1+\gamma) \]  

(3.8)

which leads to:

\[ \lambda = \frac{\ln(1+\gamma)}{\ln(1+\gamma_0)} = \frac{\ln(1+\gamma)}{\ln 2} \iff \gamma = 2^\lambda - 1 \]  

(3.9a,b)

Combining Eqs. 3.9b and 3.5 one finally obtains:

\[ \lim_{T \to \infty} \theta(\lambda, T) = \frac{2^\lambda - 1}{2^\lambda} \]  

(3.10)

The difference between the isotherms represented as function of the relative pressure and of the relative fugacity is shown in Fig 3.3 b).

Significance of the high temperature limit: In order to have \( \theta(p_0) = 0.5 \), the reference pressure \( p_0 \) must go to infinity when \( T \to \infty \), according to Eq. 3.6 b). This also means that for a fixed (and thus limited) pressure \( p \), the adsorbed amount \( \theta \) goes to zero when \( T \to \infty \). Therefore, for all practical purposes where there is an upper bound on the pressure, the lattice-gas model correctly predicts zero adsorbed amount with \( T \to \infty \). The reason for studying the high temperature limit on the rescaled isotherms, was to make sure that no condensation occurs at high temperatures and at high pressures.
2. For the case of zero cohesion, the whole system can be decomposed into non-interacting subsystems, each consisting of the adsorption sites of the same binding energy $a_i$. Therefore, the grand canonical partition function of the whole system simplifies to the product of partition functions $Q^D_{a_i}$ of these subsystems, i.e.:

$$Q^D = \prod_i Q^D_{a_i} \tag{3.11}$$

On the other hand, if $c = 0$, the canonical partition function of a subsystem with $N$ molecules adsorbed on $N^D_{sat,a_i}$ sites of binding energy $a_i$ is given by:

$$Z^D_{N,a_i} = \frac{N^D_{sat,a_i}!}{N!} \frac{e^{N^D_{sat,a_i}/kT}}{e^{N^D_{sat,a_i}/kT} - N} \tag{3.12}$$

and therefore the grand canonical partition function for each subsystem has the form:

$$Q^D_{a_i} = \left(1 + \frac{e^{a_i/kT}}{e^{a_i/kT}} \right)^{N^D_{sat,a_i}} \tag{3.13}$$

Substituting these expressions into (3.11) and applying Eq. (2.19b), the adsorption isotherm is obtained in the form:

$$\theta(\gamma) = \sum_i \frac{N^D_{sat,a_i}}{N^D_{sat,a_i}} \frac{e^{a_i/kT} \gamma}{1 + e^{a_i/kT} \gamma} \tag{3.14}$$

To express the isotherms according to the relative pressure, one uses the same relation 3.9 b) obtained for the case $T \to \infty$. This can be done since the only condition, which leads to Eq. 3.9 is that $c/kT = 0$. This condition, however, is satisfied both for $T \to \infty$ and for the present case $c = 0$. Therefore, the isotherm can be obtained in the form:

$$\theta(\lambda) = \sum_i \frac{N^D_{sat,a_i}}{N^D_{sat,a_i}} \frac{e^{a_i/kT} (2^\lambda - 1)}{1 + e^{a_i/kT} 2^\lambda} \tag{3.15}$$

Each term in the above sum corresponds to adsorption on sites of given binding energy $a_i$ and is multiplied with the frequency $N^D_{sat,a_i} / N^D_{sat}$ of adsorption sites of that binding energy.
Adsorption isotherms of the four small structures for the case $c = 0$ are given in a closed form in section 4 of Appendix III. The isotherms are completely determined by their binding energy distribution: the coefficients used in the formulas (3.27)-(3.30) of Appendix III are exactly the numbers given in the columns 2 to 7 of Table 3.1.

As equation 3.15 shows and as demonstrated in Fig. 3.4 for different values of $a/kT$, the character of the isotherms remains always of the same concave type. Independently of the type of the prefractals and of the value of $a/kT$, no steps occur. Thus, no aggregation onto adsorption sites of the same binding energy can be observed and the distribution of binding energies cannot be derived from the isotherm alone.

The isotherms can also be correlated to the parameters $N_{a, sat}^{AD} / N_{sat}^{AD}$ given in Table 3.1: structures with a higher value of $N_{a, sat}^{AD} / N_{sat}^{AD}$ show a higher adsorbed amount at the same relative pressure.

Finally, it must be noted that, since the binding energy distribution completely determines the isotherm (3.15), the latter can be generalized to arbitrary porous structures, e.g. also for the larger structures studied in Chapter 4.

**Fig 3.4** Isotherms of the four small structures at $c = 0$ and for the values $a/kT = 0.5$, 1 and 2 respectively, as indicated in the upper left picture.
Fig 3.5 Behavior of the isotherms for $a/c >> 1$ and $0 \leq a/c << 1$ at subcritical temperatures

3. The limit $a/c >> 1$ at subcritical temperatures: at subcritical temperatures the relations (3.9) does not hold anymore. However, as shown in section 2.1.3, at low enough temperatures $(c/kT \geq 2)$ the linear approximation $\gamma_{rel} \approx \lambda$ to the relative pressure is valid when $\gamma_{rel} \leq 1$. Using this approximation, it turns out that isotherms in the limit $a >> c$ (Fig 3.5) converge to the degenerated form of the Type I isotherm in the IUPAC classification (see Fig. V.1a in Appendix V). This behavior can be in fact anticipated already from the case $c = 0$ treated above under point 2 and illustrated in Fig 3.4.

4. The limit $a/c << 1$ at subcritical temperatures: isotherms in this case are represented using similarly the linear approximation $\gamma_{rel} \approx \lambda$, which is valid for $\gamma_{rel} \leq 1$. It turns out that up to the saturation pressure the adsorbed amount is very small (Fig 3.5). In order to reach the filling of the pores, the range of the relative pressure must be extended to $\lambda > 1$ in the lattice gas model. This procedure, however, raises several problems:

a) from the point of view of its interpretation: extending the relative pressure above the saturation of the bulk gas, means that extra compressive pressure is needed to fill the small pores in these structures; the liquid adsorbate must be pressed into the pores, this however violates the limits of the model.

b) from the point of view of the lattice-gas model: for $\lambda > 1$ the linear approximation may not hold anymore. One can only rely on the result of Yang and Lee [31, 32], which states that above saturation the pressure is a monotonically increasing smooth function of the fugacity.

Summarizing, for $a/c << 1$, the lattice-gas model provides an acceptable result at subcritical temperatures only in the range $\lambda \leq 1$. This, however, is sufficient since pressures above the saturation of the bulk are not of interest.
3.3 Analysis of the exactly determined adsorption isotherms

Adsorption isotherms in the general case are subject to variations in temperature, adhesion to cohesion ratio and pore geometry (Sponge-Filter, parameter m). Since the dependence on pore geometry is rather similar for all four small structures, the analysis is conducted along the variables temperature and adhesion to cohesion ratio. For the same reason, the dependence on these parameters is illustrated on isotherms, which are only qualitatively correct, while the exact isotherms are reproduced in section 5 of Appendix III.

3.3.1 Dependence on temperature

The classification of isotherms according to the temperature is made according to the sign of the second derivative $\theta''(\lambda)$. Disregarding for the moment the explicit dependence on the relative pressure, three different classes are found, as shown in Table 3.2:

1. concave isotherms: $\theta''(\lambda) < 0$ for all $\lambda$;
2. convex-concave isotherms: there exists $\lambda'$ such that $\theta''(\lambda') = 0$, $\theta''(\lambda) > 0$ for $\lambda < \lambda'$ and $\theta''(\lambda) < 0$ for $\lambda > \lambda'$;
3. two-step isotherms: there exist $\lambda'$, $\lambda''$ and $\lambda'''$ such that $\theta''(\lambda) > 0$ for $\lambda < \lambda'$ and $\theta''(\lambda)$ changes sign at $\lambda'$, $\lambda''$ and $\lambda'''$.

The isotherms of all structures undergo, with decreasing temperature, a transition from a concave to a convex-concave behavior. The appearance of the convex region and the increase in the slope of the isotherm at the inflection point $\lambda_{inf}$ is a consequence of the cohesion forces, which at lower temperatures promote the aggregation of molecules.

The transition is marked by the change in the sign of $\theta''(\lambda)$ at $\lambda = 0$ and can be studied in the parameter space $(a/c, c/kT)$. Using the expressions for $\theta''(0)$ given in section 3. of Appendix III the transition curves shown on Fig 3.6 have been found:

a) each transition curve approaches asymptotically a horizontal line in the parameter space $(a/c, c/kT)$, such that above $c/kT = \ln 2 \approx 0.69$ (or below $T = 869K$, if the assumptions of section 2.3.1 are applied) all isotherms are convex in the neighborhood of $\lambda = 0$;

b) the curves can be correlated to the geometrical properties of the corresponding porous structure:
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i) the horizontal line for $MF_1 (m=1)$ can be explained with the presence of the single adhesion type $4a$;

ii) the curves cut the vertical line at $a/c = 0$ exactly in the sequence of increasing mean adhesion contacts $N_{a,sat}^{AD}/N_{s}^{AD}$ (Table 3.1).

c) the higher the adhesion to cohesion ratio, the lower the temperature, which is needed to turn from a concave to a convex-concave behavior.

<table>
<thead>
<tr>
<th>$T = 0\ (c/kT \to \infty)$</th>
<th>$T \to \infty\ (c/kT \to 0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$MS_1 (m=1)$</td>
<td></td>
</tr>
<tr>
<td>$MF_1 (m=1)$</td>
<td></td>
</tr>
<tr>
<td>$MS_2 (m=2)$</td>
<td></td>
</tr>
<tr>
<td>$MF_2 (m=2)$</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2 The three qualitatively different types of isotherms: concave, convex-concave, and two-step isotherms in the four structures

![Graphs showing different isotherms](image)

Fig 3.6 The sign of $\theta''(0)$ in the parameter space $(a/c, c/kT)$ for the a) Menger-Sponge and the b) Menger-Filter showing the limit between the regions corresponding to convex-concave (above the curves) and concave (below the curves) isotherms.

**Two-step isotherms** occur only for the structures with $m = 2$ ($m \geq 2$, see Chapter 4). They are restricted to low temperatures and to low relative pressures and exist only above a critical adhesion to cohesion ratio. The steps correspond to a differentiated adsorption onto
adsorption sites of different binding energies in these structures: Fig 3.7. Based on the exact isotherms, the critical adhesion to cohesion ratios have been estimated to $a/c = 1.39$ and $a/c = 1.52$ for the structures $MS_i(m = 2)$ and $MF_i(m = 2)$ respectively. As the case of $MS_i(m = 1)$ shows, the presence of adsorption sites with differing binding energies is not a sufficient condition for a two-step isotherm. The pore geometry must also allow the aggregation of molecules along an edge or a plane. This can only be achieved through a higher spatial concentration of the adsorption sites of the same binding energy and with the presence of cohesion interactions.

![Graph a) The stepwise isotherm of $MS_i(m = 2)$ and the absolute partial isotherm (Eq. 2.24) of the $2a$ positions indicating the origin of the step; b) the stepwise isotherm of the $MF_i(m = 2)$ at large horizontal resolution with explanation regarding the origin of the steps.](image-url)
Chapter 3

3.3.2 Dependence of the isotherms on the adhesion to cohesion ratio in the convex-concave regime

As seen in the previous sections, for high temperatures, all isotherms approach the same concave isotherm, regardless on the adhesion to cohesion ratio. Therefore, the present analysis can be restricted to the convex-concave regime and to the limit $T \to 0$.

The dependence on $a/c$ has already been addressed in section 3.1, where the cases $a \gg c$ and $0 \leq a \ll c$ were studied. The two qualitatively different isotherms obtained there (Fig. 3.5) imply the existence of a critical adhesion to cohesion ratio. Indeed, as proven in section 6 of Appendix III, the threshold of $a/c$ to be $a/c = 0.5$ can be deduced. The proof uses a mathematical treatment of the partition function and is valid in the general case. For the small systems it results in the three cases illustrated schematically in Table 3.3 below. Exact isotherms for each structure are given in section 5 of Appendix III.

<table>
<thead>
<tr>
<th>$a/c &gt; 0.5$</th>
<th>$MS_1 (m = 1)$ and $MF_1 (m = 1)$</th>
<th>$a/c = 0.5$</th>
<th>$MS_1 (m = 2)$ and $MF_1 (m = 2)$</th>
<th>$a/c &lt; 0.5$</th>
<th>$MS_1 (m = 1)$ and $MF_1 (m = 1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\infty} &lt; 1$</td>
<td><img src="image1" alt="Graph" /></td>
<td>$\lambda_{\infty} \approx 1$</td>
<td><img src="image2" alt="Graph" /></td>
<td>$\lambda_{\infty} &gt; 1$</td>
<td><img src="image3" alt="Graph" /></td>
</tr>
<tr>
<td>$\lim_{T \to 0} \lambda_{\infty} = 0$</td>
<td><img src="image1" alt="Graph" /></td>
<td>$\lim_{T \to 0} \lambda_{\infty} = 1$</td>
<td><img src="image2" alt="Graph" /></td>
<td>$\lim_{T \to 0} \lambda_{\infty} = \infty$</td>
<td><img src="image3" alt="Graph" /></td>
</tr>
</tbody>
</table>

**Table 3.3** Dependence of the isotherms on the adhesion to cohesion ratio; the arrows show the change in the isotherms upon decrease in temperature.
The critical value of $a/c = 0.5$ can be justified as follows: from the point of view of the energy per occupied lattice site, the value of $a/c = 0.5$ in a lattice based adsorption model corresponds exactly to the periodic boundary conditions applied to a 3D lattice-gas without adsorbent. The isotherm of the latter, on the other hand, always contains the point $(\lambda = 1, \theta = 0.5)$.

The results shown in Table 3.3 can be summarized as follows:

1. The case $a/c > 0.5$ can be considered to be the one for which adhesion dominates over cohesion. The pores become filled well below the saturation pressure; with decreasing temperature, the isotherms are shifted to lower relative pressures such that the inflection point satisfies $\lim_{T \to 0} \lambda_{\text{inf}} = 0$;

2. If $a/c < 0.5$ the adsorbed amount is small up to the bulk saturation; decreasing the temperature causes the isotherms to be shifted to higher relative pressures. As demonstrated also under point 4 of section 3.2, however, the applicability of the lattice-gas model in the subcritical region is restricted to $\lambda \leq 1$;

3. At the threshold value $a/c = 0.5$ one has $\lambda_{\text{inf}} \approx 1$, regardless of the value of the temperature; moreover at $\lambda = 1$ always half of the adsorption sites are filled: $\theta(1) = 0.5$. With decreasing temperature, the slope of the isotherms at the saturation point increases, and in the limit $T \to 0$ one has:

$$\lim_{T \to 0} \theta(T, \lambda) = \frac{\lambda^{N}}{1 + \lambda^{N}},$$

as proven in section 6 of Appendix III. The values $\bar{N}$ for each structure are given in Table 3.1.

4. All porous structures follow the same scheme regarding the dependence on adhesion to cohesion ratio. Only the slopes of the isotherms at the inflection point $\lambda_{\text{inf}}$ are much steeper for $m = 2$ than for $m = 1$; this fact can be explained with the differences in the mean cohesion contacts per molecule given in Table 3.1.
3.4 Conclusions

Studying the exactly solvable cases has two main benefits:

1. one can check the results of the numerical Monte Carlo simulations for these cases if they arrive at the same result; this comparison has been performed and showed a perfect agreement between the two methods.

2. one can recognize those properties of the lattice-based adsorption model, which do not depend directly on the porous structure involved, i.e. those which can be generalized to the larger systems treated in Chapter 4:
   - For a fixed pressure \( p \) in the limit of \( T \to \infty \) the lattice-gas model predicts zero adsorption, as expected. Moreover, when represented as a function of the relative pressure, all isotherms approach, for \( T \to \infty \), the isotherm given in Eq. 3.10. This makes sure that for high enough temperatures no condensation may occur in the system. This is one of the conceptual advantages of the lattice-gas model over the BET model (see section 5.2.3 for a more detailed account). Moreover, isotherm (3.10) is valid for any discretized porous structure in the lattice model setting.
   - The isotherm (3.15) found for the case \( c/kT = 0 \) with \( a/kT > 0 \) is completely determined by the binding energy distribution of the adsorbent; therefore it can be generalized to arbitrary porous structures in the lattice-based approach. Moreover, since the isotherm (3.15) is a sum of Langmuir type isotherms, no stepwise isotherms and aggregation can be observed. For stepwise isotherms to occur the cohesion energy must be \( c > 0 \).
   - the critical adhesion to cohesion ratio \((a/c = 0.5)\) does not depend on the porous structure in the setting of the lattice-based adsorption model. Below \( a/c = 0.5 \) and at subcritical temperatures the model is limited to \( \lambda \leq 1 \), where the adsorbed amount remains always small. Since the objective of the thesis is to reproduce isotherms below bulk saturation, the more time consuming Monte Carlo simulations will only be performed for \( a/c > 0.5 \).

Summarizing, the complete description of these small systems offers a guide how to approach the adsorption in higher generation prefractals in the next chapter and also provides the range of parameters for which Monte Carlo simulations are worth to be executed.
Chapter 4 Adsorption isotherms of the large systems obtained by Grand Canonical Monte Carlo simulations

4.1 Introduction

In the present chapter results on multilayer adsorption in up to fourth generation prefractals are presented. The self-similarity of these structures extends over two orders of magnitude and allows analyzing its consequences. Adsorption isotherms have been determined by applying the Grand Canonical Monte Carlo method (Appendix IV) to the lattice-based adsorption model described in Chapter 2.

Using the information obtained by simulations, one can relate certain features, e.g. steps, of the isotherms to the adsorption onto certain categories of adsorption sites. These categories refer either to a particular pore generation or to adsorption sites with a prescribed binding energy (the so-called adhesion types).

Beside the calculation of the isotherms of the whole structure (total isotherm), the simulation method can also follow the number of molecules adsorbed at different categories of adsorption sites, giving the so-called partial isotherms, as defined in Eqs. 2.23-24.

Finally, the dependence on the adhesion to cohesion ratio and temperature is analyzed based on isotherms simulated over a wide range of parameters.
4.2 The studied structures and the range of parameters

Varying the prefractal generation \( n \) and the linear size \( m \) of the smallest pores, a total of 17 porous structures have been included in the study for both fractals, as shown in Table 4.1. Structures up to a size of \( L = 32.4 \text{ nm} \) with more than one million molecules have been analyzed in this way. Pore sizes covered the micropore range and the lower part of the mesopores, see Table 4.2. The largest pore considered belongs to the structure with \( m = 4 \) and \( n = 3 \). It has a linear size of 10.8 \text{ nm} \) and can accommodate 36 layers of water molecules.

<table>
<thead>
<tr>
<th>Sponge</th>
<th>( m = 1 )</th>
<th>( m = 2 )</th>
<th>( m = 3 )</th>
<th>( m = 4 )</th>
<th>( m = 5 )</th>
<th>( m = 6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 1 )</td>
<td>7</td>
<td>56</td>
<td>189</td>
<td>448</td>
<td>875</td>
<td>1512</td>
</tr>
<tr>
<td>( n = 2 )</td>
<td>329</td>
<td>2623</td>
<td>8883</td>
<td>21056</td>
<td>41125</td>
<td>71064</td>
</tr>
<tr>
<td>( n = 3 )</td>
<td>11683</td>
<td>93464</td>
<td>315441</td>
<td>747712</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n = 4 )</td>
<td>371441</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filter</td>
<td>( m = 1 )</td>
<td>( m = 2 )</td>
<td>( m = 3 )</td>
<td>( m = 4 )</td>
<td>( m = 5 )</td>
<td>( m = 6 )</td>
</tr>
<tr>
<td>( n = 1 )</td>
<td>12</td>
<td>96</td>
<td>324</td>
<td>768</td>
<td>1500</td>
<td>2592</td>
</tr>
<tr>
<td>( n = 2 )</td>
<td>519</td>
<td>4152</td>
<td>14013</td>
<td>33216</td>
<td>64875</td>
<td>112104</td>
</tr>
<tr>
<td>( n = 3 )</td>
<td>16743</td>
<td>133944</td>
<td>452061</td>
<td>1071552</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n = 4 )</td>
<td>490281</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 The studied structures and their saturation numbers \( N_{sat}^{3D} \)

<table>
<thead>
<tr>
<th>( k = 1 )</th>
<th>( m = 1 )</th>
<th>( m = 2 )</th>
<th>( m = 3 )</th>
<th>( m = 4 )</th>
<th>( m = 5 )</th>
<th>( m = 6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k = 2 )</td>
<td>0.3 nm</td>
<td>0.6 nm</td>
<td>0.9 nm</td>
<td>1.2 nm</td>
<td>1.5 nm</td>
<td>1.8 nm</td>
</tr>
<tr>
<td>( k = 3 )</td>
<td>0.9 nm</td>
<td>1.8 nm</td>
<td>2.7 nm</td>
<td>3.6 nm</td>
<td>4.5 nm</td>
<td>5.4 nm</td>
</tr>
<tr>
<td>( k = 4 )</td>
<td>2.7 nm</td>
<td>5.4 nm</td>
<td>8.1 nm</td>
<td>10.8 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2 The considered pore sizes as a function of pore generation \( k \) and size \( m \) of the smallest pores. The thicker line separates the micropores from mesopores.

A detailed analysis of the simulated isotherms has shown that it is sufficient to treat, for each value of \( m \), only the highest generation \( n = n_{max} (m) \) amenable for Monte Carlo simulations (see Table 4.1). This restriction is based on the following facts:

1. due to self-similarity, the features of isotherms belonging to intermediate prefractal generations, i.e. \( 1 < n < n_{max} (m) \) are completely included in the case \( n = n_{max} (m) \);
2. adsorption in the pores of generation \( k \) is only slightly affected by the presence of the pores of generation \( k + 2 \); therefore, adsorption mechanisms in the small pores and the behavior at low relative pressures does not depend considerably on \( n \) if \( n > 2 \);
3. for \( n >> 1 \) the amount adsorbed in the smaller pores (which are filled at low relative pressures) is very small compared to the volume of the larger pores; therefore, isotherms approach the Type III isotherm due to purely geometrical reasons and not because of a change in the adsorption mechanisms.

The appropriate range of the parameters \( a/c \) and \( c/kT \) has already been determined in section 2.3. For the reduced cohesion \( c/kT \) at \( T = 300 \) \( K \) the value of 2 was adopted, while for the adhesion to cohesion ratio the range \( 0 < a/c < 3 \) has been taken. The consequences of zero cohesion have already been analyzed in Chapter 3, section 3.2.

<table>
<thead>
<tr>
<th>Adhesion to cohesion ratio</th>
<th>Weak adhesion</th>
<th>Strong adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a/c )</td>
<td>1.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduced cohesion and temperature</th>
<th>Theoretically relevant</th>
<th>Relevant for practice</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c/kT )</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>( T )</td>
<td>327°C</td>
<td>127°C</td>
</tr>
</tbody>
</table>

Table 4.3 The studied range of adhesion to cohesion ratio and reduced cohesion with the corresponding temperatures.

The final range of \( 1 \leq a/c \leq 3 \) for the adhesion to cohesion ratio has been established based on the following considerations:

1. adsorption in statistically self-similar building materials corresponds to the strongly hydrophilic case, therefore it is reasonable to assume that \( a/c \geq 1 \);
2. test isotherms performed in the range \( a/c < 1 \), were not of interest for two reasons:
   - up to about a relative humidity of 80\%, i.e. in the range where the study of self-similarity would be of interest, no adsorption could be observed;
   - calculated isotherms did not show considerable adsorbed amount even at saturation pressure and it is suspected that equilibrium is not reached here by the Monte-Carlo method; for, it is known that with successively larger structures and pores one approaches the thermodynamic limit in the lattice-gas model, where the effect of the surface is negligible and the phase transition must occur exactly at the saturation pressure; in the simulation method, however, the low value of adhesion compared to cohesion is not sufficient to initiate adsorption on the surface and leads to wrong results close to the saturation pressure. This limitation of the Monte Carlo method is of a numerical nature, see the “critical slowing down” effect [55].
3. for \( a/c \geq 3 \) isotherms did not change significantly with the adhesion to cohesion ratio. For each of the 34 structures a total of 30 isotherms have been computed, corresponding to all possible combinations of \( c/kT \) and \( a/c \) given in Table 4.3. In the range \( 1.8 \leq c/kT \leq 2.2 \) the isotherms did not show any qualitative changes, therefore the study has been mainly reduced to the case \( c/kT = 2 \).

4.3 Results obtained by Monte Carlo simulations

The results obtained by Monte Carlo simulations are comprised in Table 4.4, which shows side by side the characteristics of the Sponge and the Filter and emphasizes the following hierarchy of dependencies from the various parameters:

1. **Influence of pore geometry**: the interplay between pore geometry and the cohesion interactions in the two structures results in the qualitatively different isotherms, as reproduced in Figs 4.1 b), 4.2 b), Tables 4.10-11, and as discussed further in Table 4.5.

2. **Influence of the parameter \( m \)**: the parameter \( m \) generates, on the level of total isotherms, a classification into a microporous \( (m \leq 3) \) and mesoporous group \( (m \geq 4) \) for both the Filter and the Sponge; however, as explained in Fig. 4.4 and Table 4.6 below, there are different reasons which lead to the same classification. Therefore, the pore partial isotherms of the Filter are subject to the same classification into a micro- and mesoporous group, while those of the Sponge depend essentially only on the pore size, irrespective of the value of \( m \).

3. **Influence of the adhesion to cohesion ratio**: the dependence on the adhesion to cohesion ratio has been analyzed on the level of total isotherms for the micro- and mesoporous group, as well as for the pore partial isotherms of the two structures, as shown in Table 4.4 and in Tables 4.7-9 respectively.

4. **The temperature dependence** of isotherms has been analyzed for \( 2.2 \geq c/kT \geq 1.5 \), i.e. in the temperature range \( 0^\circ C \ldots 127^\circ C \) respectively, as shown in Fig 4.5 and Table 4.12. Additionally, the temperature dependence of the estimated surface area has also been studied. For this purpose the Point B method has been chosen: the estimation of monolayer coverage proceeds by locating the point of maximal curvature of the isotherm in the low pressure region, as illustrated on Fig 4.6 for the micro and the mesoporous group. The results of this analysis are comprised in Figs. 4.7-8 and Tables 4.13-14 respectively.
Conventions: populations are denoted as follows:
- \( p_1, p_2, \ldots, p_n \) for the pore generations 1 \( \ldots \) \( n \)
- \( 4a, 3a, 2a, la, 0a \) for the adhesion types
- \((ia, pj)\) for the adhesion type \( ia \) in the \( j^{th} \) pore generation

<table>
<thead>
<tr>
<th>Fundamental property</th>
<th>Menger-Sponge</th>
<th>Menger-Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Independent adsorption in each pore generation:</td>
<td>- strictly porewise adsorption for ( a/c = 1 ) : Fig 4.1</td>
<td>Correlation between adsorption in different pores:</td>
</tr>
<tr>
<td>(determined by the generating procedure and the fractal dimension)</td>
<td>- correlations are due to the presence of Type A and Type B pores, as</td>
<td>- correlations are due to the presence of Type A and Type B pores, as</td>
</tr>
<tr>
<td></td>
<td>illustrated for ( a/c = 1 ) in Figs 4.2-3 a)</td>
<td>illustrated for ( a/c = 1 ) in Figs 4.2-3 a)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pore partial isotherms</th>
<th>see Table 4.7</th>
<th>see Tables 4.8-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>role of the geometric parameters ( m ) and pore size ( r )</td>
<td>( - m ) determines the size of the smallest pores only</td>
<td>( - m ) determines the size of the smallest pores only</td>
</tr>
<tr>
<td></td>
<td>( - ) isotherms depend only on the pore size ( r )</td>
<td>( - ) isotherms depend only on the pore size ( r )</td>
</tr>
<tr>
<td>dependence on ( a/c )</td>
<td>( r \leq 0.6 \text{ nm} ) pores become filled at very low relative pressures ( \rightarrow ) pore filling mechanism</td>
<td>( r \leq 0.9 \text{ nm} ) pores become filled at very low relative pressures ( \rightarrow ) pore filling mechanism</td>
</tr>
<tr>
<td></td>
<td>( 0.9 \text{nm} \leq r \leq 1.5 \text{nm} ) ( 1 &lt; a/c &lt; 2 ) : transition at a critical ( a/c ) is related to the filling of the central pore of the MS : Fig 4.3 b)</td>
<td>( 1.8 \text{nm} \leq r \leq 2.7 \text{nm} ) (four regions as marked in Table 4.8)</td>
</tr>
<tr>
<td></td>
<td>( a/c \geq 3 ) : the second step corresponds to the filling of the central pore</td>
<td>region 2: completion of the monolayer concomitantly with the ( 0a ) positions connecting the isolated islands on the ill-defined surface (extended monolayer)</td>
</tr>
<tr>
<td></td>
<td>( r \geq 1.8 \text{nm} ) ( 1 &lt; a/c &lt; 3 ) : adsorption in the sequence of adhesion types: ( 2a \rightarrow la \rightarrow 0a )</td>
<td>region 3: volume filling of Type A pores: Fig 4.2 a)</td>
</tr>
<tr>
<td></td>
<td>( a/c \geq 3 ) : horizontal plateau corresponds to the completed monolayer: ( (2a + 1a) \rightarrow 0a )</td>
<td>region 4: volume filling of Type B pores: Fig 4.2 a)</td>
</tr>
<tr>
<td></td>
<td>( (2a + 1a) \rightarrow 0a ) means that no differentiation into steps can be observed between adsorption to these positions.</td>
<td>( r \geq 5.4 \text{nm} ) similar to the case ( 1.8 \text{nm} \leq r \leq 2.7 \text{nm} ) but volume effects dominate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total isotherms</th>
<th>see Table 4.10</th>
<th>see Table 4.11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microporous group: ( m \leq 3 ) dependence on ( a/c )</td>
<td>( 1 &lt; a/c &lt; 3 ) ( \rightarrow ) completion of the monolayer in the higher pores smoothens the steps of the first two pore generations ( a/c \geq 3 ) : horizontal plateau includes the completed monolayer and the volume of the smallest pores: ( \rightarrow )</td>
<td>( 1 &lt; a/c ) ( \rightarrow ) adsorption in the sequence of adhesion types: ( 2a \rightarrow la \rightarrow 0a ) ( a/c \geq 3 ) : horizontal plateau corresponds to the completed monolayer: ( (2a + 1a) \rightarrow (0a, p3) \rightarrow (0a, p4) )</td>
</tr>
<tr>
<td></td>
<td>( (4a + 2a + 1a + p1 + p2) \rightarrow (0a, p3) \rightarrow (0a, p4) )</td>
<td>( (4a + 2a + 1a + p1 + p2) \rightarrow (0a, p3) \rightarrow (0a, p4) )</td>
</tr>
<tr>
<td>Mesoporous group: ( m \geq 4 ) dependence on ( a/c )</td>
<td>( 1 &lt; a/c &lt; 3 ) ( \rightarrow ) adsorption in the sequence of adhesion types: ( 2a \rightarrow la \rightarrow 0a ) ( a/c \geq 3 ) : horizontal plateau corresponds to the completed monolayer: ( (2a + 1a) \rightarrow (0a, p1) \rightarrow (0a, p2) )</td>
<td>( 1 &lt; a/c &lt; 3 ) ( \rightarrow ) adsorption in the sequence of adhesion types: ( 2a \rightarrow la \rightarrow 0a ) ( a/c \geq 3 ) : horizontal plateau corresponds to the completed monolayer: ( (2a + 1a) \rightarrow 0a ) ( \rightarrow )</td>
</tr>
<tr>
<td></td>
<td>( r \geq 1.8 \text{nm} ) ( a/c \geq 3 ) : horizontal plateau corresponds to the completed monolayer: ( (2a + 1a) \rightarrow (0a, p1) \rightarrow (0a, p2) )</td>
<td>( r \geq 1.8 \text{nm} ) ( a/c \geq 3 ) : horizontal plateau corresponds to the completed monolayer: ( (2a + 1a) \rightarrow 0a ) ( \rightarrow )</td>
</tr>
</tbody>
</table>

Table 4.4 Results obtained by Monte Carlo simulation
Chapter 4

**Table 4.5** The consequences of pore geometry for the two structures

<table>
<thead>
<tr>
<th>Relevant property determined by $m$</th>
<th>Effect on adsorption</th>
<th>Consequence for monolayer estimation for $a/c \geq 3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$MS$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>the size of the smallest pores</td>
<td>pore partial isotherms depend only on pore size</td>
<td>$m \leq 3$: overestimation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$m \geq 4$: good estimate</td>
</tr>
<tr>
<td>$MF$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>the surface structure of the pores (Fig 4.4)</td>
<td>for $m \leq 3$, cohesion does not contribute to the completion of the monolayer, since the surface structure prevents the molecules from direct contact</td>
<td>$m \leq 3$: underestimation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$m \geq 4$: good estimate</td>
</tr>
</tbody>
</table>

**Table 4.6** Role of the parameter $m$ in the two structures

<table>
<thead>
<tr>
<th>Geometric property</th>
<th>Effect on adsorption</th>
<th>Consequence on isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$MS$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pores of the same size and sites of the same binding energy are closely grouped together</td>
<td>enhanced adsorption at well-defined pressures due to cohesion</td>
<td>- well-defined steps;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$MF$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pores and surfaces are poorly defined, pores of the same size are separated both by smaller and larger pores</td>
<td>the ability of cohesion interactions to build aggregates is weakened by the pore structure</td>
<td>- poorly defined steps;</td>
</tr>
</tbody>
</table>

**Fig 4.1** a) Cross-section along a plane parallel to an external face of the $MS$: black colored regions correspond to the solid material, gray areas to consecutive pore generations and dashed lines to the limits between pore generations; b) Total isotherm and absolute partial isotherms (see Eq. 2.24) of pore generations $k = 1$ to $k = 4$ of $MS_4 (m = 1)$ for $a/c = 1$. 

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**Fig 4.2** a) Cross-section along a plane parallel to an external face of the MF showing the location of Type A and Type B pores; b) Total isotherm and absolute partial isotherms (see Eq. 2.24) of pore generations $k = 1$ to $k = 4$ of $MF_4(m = l)$ for $a/c = 1$.

**Fig 4.3** a) Correlations between the relative pore partial isotherms (see Eq. 2.23) of the MF for $a/c = 1$; b) transition in the pores of size $0.9nm \leq r \leq 1.5nm$ of the MS in the range $1 \leq a/c \leq 2$.

<table>
<thead>
<tr>
<th></th>
<th>$m = 1, k = 2$</th>
<th>$m = 3, k = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Menger-Sponge</td>
<td><img src="image" alt="Menger-Sponge m=1 k=2" /></td>
<td><img src="image" alt="Menger-Sponge m=3 k=1" /></td>
</tr>
<tr>
<td></td>
<td>$\alpha = 1.375$</td>
<td>$\alpha = 1.666$</td>
</tr>
<tr>
<td>Menger-Filter</td>
<td><img src="image" alt="Menger-Filter m=1 k=2" /></td>
<td><img src="image" alt="Menger-Filter m=3 k=1" /></td>
</tr>
<tr>
<td></td>
<td>$\alpha = 0$</td>
<td>$\alpha = 1.33$</td>
</tr>
</tbody>
</table>

**Fig 4.4** Internal surface of the pores in the two structures showing the effect of the parameter $m$: light and dark gray squares correspond to 1a and 2a positions respectively; $\alpha$ gives the mean number of cohesion connections per molecule in a completely filled monolayer on these surfaces.
Table 4.7
Menger-Sponge: relative pore partial isotherms and their dependence on $a/c$; $r$ denotes the pore size, $\theta a-2a$ stay for the adhesion types

<table>
<thead>
<tr>
<th>$a/c$</th>
<th>$r \leq 0.6 \text{ nm}$</th>
<th>$0.9 \text{ nm} \leq r \leq 1.5 \text{ nm}$</th>
<th>$r \geq 1.8 \text{ nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1,2 \text{ molecules}$</td>
<td>$3,4,5 \text{ molecules}$</td>
<td>$&gt;5 \text{ molecules}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$a/c=1$</th>
<th>$a/c=2$</th>
<th>$a/c=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{ref}$</td>
<td>$\theta_{ref}$</td>
<td>$\theta_{ref}$</td>
</tr>
<tr>
<td>$p/p_0$</td>
<td>$p/p_0$</td>
<td>$p/p_0$</td>
</tr>
</tbody>
</table>

$r < 0.6 \text{ nm}$
$0.9 \text{ nm} < r < 1.5 \text{ nm}$
$r > 1.8 \text{ nm}$
Table 4.8

Menger-Filter: relative pore partial isotherms and their dependence on $a/c$

I Microporous case: $m \leq 3$

<table>
<thead>
<tr>
<th></th>
<th>$a/c=1$</th>
<th>$a/c=2$</th>
<th>$a/c=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r \leq 0.9 nm$</td>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
<tr>
<td>$1.8 nm \leq r \leq 2.7 nm$</td>
<td><img src="image4.png" alt="Graph" /></td>
<td><img src="image5.png" alt="Graph" /></td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
<tr>
<td>$r \geq 5.4 nm$</td>
<td><img src="image7.png" alt="Graph" /></td>
<td><img src="image8.png" alt="Graph" /></td>
<td><img src="image9.png" alt="Graph" /></td>
</tr>
</tbody>
</table>
Table 4.9
Menger-Filter: relative pore partial isotherms and their dependence on $a/c$; $0a-2a$ stay for the adhesion types

II Mesoporous case: $m \geq 4$

<table>
<thead>
<tr>
<th></th>
<th>$a/c=1$</th>
<th>$a/c=2$</th>
<th>$a/c=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r \leq 1.8 \text{ nm}$</td>
<td><img src="#" alt="Graph" /></td>
<td><img src="#" alt="Graph" /></td>
<td><img src="#" alt="Graph" /></td>
</tr>
<tr>
<td></td>
<td>$\theta_{rel}$</td>
<td>$\theta_{rel}$</td>
<td>$\theta_{rel}$</td>
</tr>
<tr>
<td></td>
<td>$p/p_0$</td>
<td>$p/p_0$</td>
<td>$p/p_0$</td>
</tr>
<tr>
<td>$r \geq 3.6 \text{ nm}$</td>
<td><img src="#" alt="Graph" /></td>
<td><img src="#" alt="Graph" /></td>
<td><img src="#" alt="Graph" /></td>
</tr>
<tr>
<td></td>
<td>$\theta_{rel}$</td>
<td>$\theta_{rel}$</td>
<td>$\theta_{rel}$</td>
</tr>
<tr>
<td></td>
<td>$p/p_0$</td>
<td>$p/p_0$</td>
<td>$p/p_0$</td>
</tr>
</tbody>
</table>
Table 4.10
Menger-Sponge: total isotherms and their dependence on a/c
0a-2a stay for the adhesion types, 1p-4p denote the pore generations

<table>
<thead>
<tr>
<th></th>
<th>a/c=1</th>
<th>a/c=1.5</th>
<th>a/c=2</th>
<th>a/c=3</th>
</tr>
</thead>
<tbody>
<tr>
<td>microporous</td>
<td><img src="image1" alt="Microporous" /></td>
<td><img src="image2" alt="Microporous" /></td>
<td><img src="image3" alt="Microporous" /></td>
<td><img src="image4" alt="Microporous" /></td>
</tr>
<tr>
<td>group: m ≤ 3</td>
<td><img src="image1" alt="Microporous" /></td>
<td><img src="image2" alt="Microporous" /></td>
<td><img src="image3" alt="Microporous" /></td>
<td><img src="image4" alt="Microporous" /></td>
</tr>
<tr>
<td>mesoporous</td>
<td><img src="image5" alt="Mesoporous" /></td>
<td><img src="image6" alt="Mesoporous" /></td>
<td><img src="image7" alt="Mesoporous" /></td>
<td><img src="image8" alt="Mesoporous" /></td>
</tr>
<tr>
<td>group: m ≥ 4</td>
<td><img src="image5" alt="Mesoporous" /></td>
<td><img src="image6" alt="Mesoporous" /></td>
<td><img src="image7" alt="Mesoporous" /></td>
<td><img src="image8" alt="Mesoporous" /></td>
</tr>
</tbody>
</table>
Table 4.11
Menger-Filter: total isotherms and their dependence on a/c (isotherms of MS are reproduced using dashed curves)

<table>
<thead>
<tr>
<th></th>
<th>a/c=1</th>
<th>a/c=2</th>
<th>a/c=3</th>
</tr>
</thead>
<tbody>
<tr>
<td>microporous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>group: m &lt; 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image1" alt="Graph" /></td>
<td><img src="image2" alt="Graph" /></td>
<td><img src="image3" alt="Graph" /></td>
</tr>
<tr>
<td>mesoporous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>group: m ≥ 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image4" alt="Graph" /></td>
<td><img src="image5" alt="Graph" /></td>
<td><img src="image6" alt="Graph" /></td>
</tr>
</tbody>
</table>
Chapter 4

Temperature dependence

\[ m=1 \quad n=4 \quad \alpha/c=1.25 \]

\[ c/kT=2.2 \]

\[ P/P_0 \]

a) b)

Fig 4.5 Temperature dependence of adsorption isotherms of the Sponge and Filter for a) \( \alpha/c=1.25 \) and b) \( \alpha/c=3 \). The adsorption isotherms correspond from right to left to the values \( c/kT = 1.5, 1.8, 2, 2.2 \), i.e., for \( T = 127, 60, 27, 0°C \) respectively.

Effect of lowering the temperature - adsorbed amount increases at the same relative pressure over the whole range of humidities

Effect of increasing the temperature - isotherms are smoothened and lose their finer details

Table 4.12 Temperature dependence of isotherms

<table>
<thead>
<tr>
<th>Microporous group</th>
<th>m=1</th>
<th>( \alpha/c=3 )</th>
<th>( c/kT=2 )</th>
<th>MS</th>
<th>MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous group</td>
<td>m=6</td>
<td>( \alpha/c=3 )</td>
<td>( c/kT=2 )</td>
<td>MS</td>
<td>MF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig 4.6 Illustration for the point B method; a comparison of the total isotherms with the absolute partial isotherm of the monolayer shows the accuracy of the estimation for the a) microporous and the b) mesoporous case.
Fig 4.7 The ratio $F$ of the estimated to the real monolayer coverage as a function of temperature and adhesion to cohesion ratio for $m=1$; the curves correspond consecutively to the values $a/c = 1.25, 1.5, 1.75, 2, 3$.

Fig 4.8 The ratio $F$ of the estimated to the real monolayer coverage for the mesoporous group as a function of temperature;

<table>
<thead>
<tr>
<th>Estimation of surface area: general features</th>
<th>Microporous case $m \leq 3$</th>
<th>Mesoporous case $m \geq 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applicability of the method</td>
<td>applicable for $a/c &gt; 1$:</td>
<td>applicable only for $a/c \geq 3$</td>
</tr>
<tr>
<td></td>
<td>- $a/c \approx 1$: Point B not defined</td>
<td>- $a/c \approx 1$: Point B not defined</td>
</tr>
<tr>
<td></td>
<td>- $1 &lt; a/c &lt; 3$: Point B not defined unequivocally</td>
<td></td>
</tr>
<tr>
<td>Quality of the estimate</td>
<td>bad estimates:</td>
<td>good estimates:</td>
</tr>
<tr>
<td></td>
<td>- underestimation with more than 60%;</td>
<td>- error less than 5% at $c/kT = 2$;</td>
</tr>
<tr>
<td></td>
<td>- overestimation with 20%</td>
<td>- error less than 15% for $c/kT \geq 1.5$</td>
</tr>
<tr>
<td>Dependence of the estimate on temperature</td>
<td>increases with decreasing temperature; does not become more accurate in general;</td>
<td>increases and becomes more accurate with decreasing temperature</td>
</tr>
<tr>
<td>Dependence of the estimate on $a/c$</td>
<td>increases with increasing $a/c$; no improvement of accuracy in general;</td>
<td>increases and becomes more accurate with increasing $a/c$;</td>
</tr>
<tr>
<td>Differences Sponge versus Filter</td>
<td>important differences</td>
<td>no differences for the two structures</td>
</tr>
</tbody>
</table>

Table 4.13 General features regarding the estimation of surface area
### Table 4.14 Estimation of surface area for the microporous group

<table>
<thead>
<tr>
<th>Surface area for the microporous group</th>
<th>Menger Sponge</th>
<th>Menger Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stability of the estimate</td>
<td>large variations of the estimate for $a/c \geq 2$ in the range $1.6 \leq c/kT \leq 1.8$</td>
<td>stable estimates; larger variation only for $a/c \geq 3$ in the range $1.8 \leq c/kT \leq 2$</td>
</tr>
</tbody>
</table>
| Quality of the estimate               | - underestimation with 60 - 70% for $a/c < 2$  
- overestimation with 20% for $a/c \geq 3$ | - underestimation with 60 - 85% for $a/c < 3$  
- error less than 10% for $a/c \geq 3$ |
Chapter 5 Discussion and Conclusions

5.1 Results

5.1.1 The combined effect of cohesion and pore structure on adsorption

The present work considers cohesion interactions as well as 3D porosity in the adsorption model. The corresponding results can be summarized as follows:

The case \( c=0 \): if cohesion interactions are neglected, the binding energy distribution completely determines the isotherm (Eq. 3.15), while pore structure does not have any effect. Therefore, the isotherms of the Menger Sponge and the Filter do not differ considerably. The presence of different binding energies in these structures does not lead to stepwise isotherms in this case.

**Menger Sponge, \( c>0 \):** for the MS adsorption isotherms with clearly defined steps have been found (Table 4.10). These steps indicate that the filling of adsorption sites corresponding to different populations (pore generations or adhesion types) occurs by aggregation at well-defined relative pressures. This also means that any two pairs of populations become filled independently.

**Menger Filter, \( c>0 \):** the isotherms of the MF, on the other hand, are quite smooth and almost S-shaped, such that no populations can directly be identified (Table 4.11). As shown in Fig 4.3 a), the adsorption in different pore generations is strongly correlated.

**Influence of pore geometry:** the pore structure can both promote and destroy the building of aggregates of adsorbed molecules. Therefore the presence of cohesion is a necessary but not sufficient condition in order to have stepwise isotherms. Determining factors in this sense are the following:

1. **Pore topology:** the building of 3D aggregates (pore filling) is determined by the way pores of different sizes are interconnected: in the Sponge pores of the same size are strongly grouped together, while those of different size are weakly connected. This favors the building of aggregates in consecutive pore generations. On the other hand, in the Filter, pores of the same generation do not link by cohesion and therefore prevent the building of aggregates. This difference between
the two structures can be characterized quantitatively by the parameter \( \Delta_{\alpha,k} \)
introduced in section 1.3.4. Assuming pore sizes in the two structures to be equal, it has been shown that the cohesion boundary per unit volume in the smallest pores is about seven times larger in the Filter than in the Sponge (Fig 1.10), while for the other pore generations this ratio lies between 6.47 and 7.

2. **Surface structure**: the quality of the internal surfaces of the pores has a similar role in promoting or destroying the building of aggregates. With respect to the 1D aggregation to \( 2a \) positions as well as the 2D aggregation to \( la \) positions, the parameter \( m \) plays a different role in the two structures. For the Sponge, both 1D and 2D aggregation are possible independently of \( m \). In the Filter, on the other hand, this is visible only for \( m \geq 4 \). From this point of view the surfaces can be characterized by computing the mean number \( \alpha \) of cohesion contacts in a completely filled monolayer. Fig 4.4 illustrates for instance that in the Menger-Filter for \( m=1 \) no cohesion interactions are involved in the saturation of the monolayer.

5.1.2 The role of self-similarity in adsorption

**Consequences of self-similarity**: since prefractals of a given generation \( n>1 \) contain all those of lower generation \( k=1...n-1 \), it is expected that the corresponding isotherms show a similar repetitive pattern. Indeed, the isotherm of \( MS_{n-1}(m) \) contains, upon a rescaling, the isotherm of the lower generation prefractal \( MS_{n}(m) \). Moreover, if \( a/c=1 \), the saturation of the Menger-Sponge proceeds porewise: Fig 4.1, such that the heights of the steps correspond actually to the pore size distribution. For the Menger Filter, on the other hand, this scaling property is disturbed by correlations between pore generations. A repetitive pattern due to self-similarity can only be observed here on the level of relative pore partial isotherms: Fig. 4.3. It must also be noted that starting with \( n=10 \) volume effects dominate, such that the property of self-similarity is not relevant anymore.
5.1.3 The reliability of the estimated monolayer coverage

The Point B method for the estimation of the monolayer coverage has been applied to the adsorption isotherms obtained by Monte Carlo simulations. Through this analysis one could identify the influence of adhesion energy, surface structure and temperature on the accuracy of this estimation, and under which conditions one can expect a reliable estimate. The results of this study are comprised below:

1. **Good estimates:** for \( m \geq 4 \) both structures returned estimates with an error less than 5% in the temperature range of interest, i.e. around \( c/kT \approx 2 \), see Fig 4.8. The method could be applied for the case of strong adhesion (\( \alpha/c \geq 3 \)), i.e. where the Point B was unequivocally defined: Fig 4.6 b)

2. **Bad estimates:** for \( m \leq 3 \) the estimate varied between 15% to 120% of the real monolayer coverage depending on the various parameters: Fig 4.7 a).
   a) For the Menger-Sponge the low value of \( m \) manifests itself in the presence of small pores (less than four molecular diameters wide), which promote the building of aggregates; therefore the estimate actually measures their volume instead of monolayer coverage: for \( 1.25 \leq \alpha/c \leq 1.75 \) it gives the volume of the first generation pores and leads to an underestimation with 60%; for \( \alpha/c \geq 3 \) the volume of the \( k = 2 \) pores is included too, such that the monolayer coverage is overestimated with 20%: Fig 4.6.a)
   b) For the Menger Filter the low value of \( m \) destroys the ability of the lateral interactions to build aggregates, and therefore the monolayer coverage is underestimated with up to 80%, for \( \alpha/c \geq 3 \) better estimates are obtained and overestimation is not possible.

3. **Temperature dependence:** for \( m \geq 4 \), the estimate only slightly varies with temperature; in contrast, low variability does not always mean a good estimate, as shown in Fig. 4.7 for the microporous case \( m \leq 3 \). Sudden changes with temperature occur in the Menger-Sponge for \( \alpha/c \geq 2 \) with \( 1.6 \leq \alpha/c \leq 1.8 \) as well as for the Filter at \( \alpha/c \geq 3 \) with \( 1.8 \leq \alpha/c \leq 2 \).
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5.2 Comparison with the literature

5.2.1 Stepwise versus S-shaped isotherms

The Menger Sponge and Filter reproduce two important classes of isotherms studied in the literature, i.e. the stepwise Type VI and the S-shaped Type IV isotherm (Fig V.1 a). They provide an alternative explanation for the adsorption processes, which lead to these types of isotherms.

1. Stepwise isotherms: in the literature the steps are most often attributed to the building of consecutive layers of adsorbed molecules [56]. This explanation is based on the fact that the step heights are approximately equal and on the assumption that the surface of the pores is reasonably flat. Theoretical studies on lattice-gas models [57] predict that the following conditions must be satisfied in order to have stepwise isotherms:
   - C1: lateral interactions between adsorbed molecules;
   - C2: energetic homogeneity of the surface;
   - C3: long-range adhesion interactions.

The Menger Sponge provides an alternative explanation to stepwise isotherms, where the steps correspond to the consecutive filling of pore generations. According to these results a stepwise isotherm may also be the consequence of the discrete pore size distribution of the adsorbate, as well as its ability to promote aggregation. Additionally, in the present case only the presence of lateral interactions is important, while conditions C2 and C3 must not necessarily be satisfied.

2. S-shaped isotherms are interpreted in the literature in two possible ways:
   - in the same theoretical setting of lattice-gas models [57] it has been shown that lifting condition C2, i.e. introducing surface energetic heterogeneity destroys these steps and leads to S-shaped isotherms [58].
   - in the BET theory, the S-shaped isotherm is a consequence of the fact the lateral interactions are neglected and one has a well-defined flat surface.

The example of the Menger Filter shows that not only energetic heterogeneity of the surface or the absence of lateral interactions can lead to S-shaped isotherms. Surface structures with a low \( \alpha \) value (in the sense of Fig 4.4) and non-connectedness of pores of the same generation (in the sense of set-theory) destroys the effect of lateral interactions and leads to S-shaped
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isotherms. This also explains the apparent success of the BET model in the low pressure region \(0.05 \leq \frac{p}{p_0} \leq 0.3\) [1].

Additionally, the BET model has also been used extensively in the study of water adsorption in cement [27]. However, for this material the condition of large well-defined surfaces (as postulated in the BET theory) can hardly be accepted.

The example of the Menger Filter also shows that a discrete pore size distribution does not always imply a stepwise isotherm, but may also lead to S-shaped isotherms. It is also worth to mention here that recent experiments using NMR relaxation [59] brought evidence that the pore size distribution of hydrated cement is discrete in the lower meso range. Therefore, the Menger-Filter could provide a possible explanation for the structure of cement and for adsorption processes leading to S-shaped isotherms.

5.2.2 Relation to other approaches to self-similarity

The fractal BET theory

The first step in the theoretical study of adsorption on self-similar adsorbents was the extension of the BET theory to fractal structures [25]. The isotherm has been obtained in a closed form, incorporating the fractal dimension as an additional parameter. This approach, however, can be criticized in the following way:

- it is implicitly assumed the self-similarity of the porous structure to be similar to that of mathematical fractals; however, there is experimental evidence [60] that most objects of the physical reality show a self-similarity extended over at most two orders of magnitude;
- if self-similarity has only a short range, then the discrete character of prefractals (pore sizes form a limited geometric sequence) has to be taken into account; therefore the existing mathematical apparatus of fractal geometry cannot be used to deduce the fractal BET isotherm;
- results presented in this thesis show that fractal dimension alone does not uniquely determine the qualitative aspect of the isotherm. Therefore, it is not possible to determine the fractal dimension from the isotherm alone as done for example in [6].
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**Pore topology and fractal models**

Theoretically constructed self-similar objects may help to gain an insight into porous structures [16]. They constitute a challenge to the rather simple definitions used in the recommendations of IUPAC for the characterization of porous solids [29]. The usefulness of the fractal approach to catalysts has been questioned by Conner et al. [17], who analyzed the geometry of the Menger-Sponge and found that it has a rather low connectivity, according to their definition. The authors arrived to the conclusion that fractals in general cannot reflect the void networks or real catalysts. The present example of the Menger-Filter, however, shows that 3D self-similar structures can encompass a much broader class of porous structures.

5.2.3 **Temperature dependence of adsorption**

**Temperature dependence of adsorption isotherms**

Isotherms measured at different temperatures are not only used for computing quantities related to adsorption (e.g. the isosteric heat of adsorption [61] p. 44), they may also provide the key for the understanding of the adsorption process, as demonstrated for example in [62]: following the changes of step heights with temperature (see Fig V.1 b), the authors deduce that the adsorption of water on silica proceeds in a layerwise fashion.

The temperature dependence of the isotherms of water in cement has been investigated by Badmann [63]. At lower temperatures the adsorbed amount increases in the hygroscopic region and decreases in the capillary region: Fig V.2.b). The results of this thesis are restricted to the hygroscopic range where they predict, similarly, an increase of the adsorbed amount with decreasing temperature.

**Temperature dependence in multilayer models of adsorption theory**

In order to understand the effects of temperature variation on adsorption, models showing qualitatively correct temperature dependence are required. The most frequently used BET model, however, fails to predict the adsorption at different temperatures for several reasons:

1. its parameters must be adjusted at each temperature [63];
2. although it describes multilayer adsorption, the model does not include a critical temperature;
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3. the saturation pressure of the gas is defined as the pressure at which an infinite number of layers adsorb on the surface, i.e. the saturation pressure is ultimately bound to the presence of this surface and not only to the properties of the adsorptive;

4. as a consequence, for $T \to \infty$ the BET theory still predicts the building of an infinite number of layers on the adsorbate at this saturation pressure;

Therefore, the BET theory fails to give a qualitative correspondence with the real situation. The generalized lattice gas model, on the other hand, does not show the inconsistencies mentioned above under points 2-4.

Temperature dependence of the estimation of monolayer coverage

Although theoretical investigations on the accuracy of the BET estimation have been performed for surface fractals [64, 65], to our knowledge, no author dealt before with the temperature dependence of this estimation. Although the method of monolayer estimation was originally developed for the case of nitrogen adsorption at its liquefaction temperature ($T = 77K$), the BET model alone does not specify the temperature at which the method would lead a reliable estimate of the monolayer coverage.

The main problem in this respect is that the real internal surface of the adsorbent basically does not change in the temperature range of interest. The shape of the isotherms, on the other hand, changes with temperature. If the BET method was correct, it should return the same surface area at different temperatures. Actually, there are large differences between cement surface areas estimated by different authors [27].

The accuracy of the BET estimation has been tested by applying the method on adsorption isotherms simulated at different temperatures. This analysis could identify the influence of various factors on the quality of the estimation, as described in section 4.3. Without a priory knowledge about the porous structure (pore sizes, surface roughness), the following predictions can be made based on the temperature dependence of the estimated monolayer coverage:

a) large variability (more than 100% at lower temperatures) points towards an adsorbent, which promotes the building of aggregates and to the presence of micropores; in this case one has a bad estimate;

b) conversely, the low variability with temperature does not necessarily imply a good estimation of monolayer coverage;
c) if the internal surface is build up from patches of size larger than four molecular
diameters the estimation is reliable.

5.3 Conclusions

1. The adsorption in the Menger-Filter and Sponge provides an alternative to the building
up of layers associated with stepwise and S-shaped isotherms in the literature.
2. Fractal dimension alone cannot account for the qualitative features of the isotherms.
   Beside fractal dimension, there are several other properties, which must be taken into
   account. In this sense one could mention the property of “lacunarity” [3, 66] or the
   cohesion boundary introduced in this thesis.
3. The results suggest that the pore topology of the prefractal structures, as described by
   the parameter $\Delta_{n,k}$, characterizes their ability to promote/destroy the building of
   aggregates and thereby determines the qualitative aspect of adsorption.
4. Self-similarity has an effect on the isotherm mostly in the micro and mesopore range
   and therefore at low pressures. In consequence the relative low range of self-similarity
   (as observed in the literature [60]), readily shows its effects on the isotherms.
5. Adsorption isotherms simulated at different temperatures provide a reference for the
   understanding of experimental isotherms. They also may contribute to the refinement of
   existing adsorption theories and methods to deduce properties of the porous structures
   from their isotherms.
Appendix I Formulas: geometric properties of the Menger Sponge and Filter

The table below contains the formulas for the geometric quantities of prefractals of generation \( n \) and linear size \( L \). The pore generations are indexed by \( k = 1 \ldots n \) starting with the smallest pores.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Menger-Sponge</th>
<th>Menger-Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore widths ( l_k ), where ( k = 1 \ldots n )</td>
<td>( l_k = \frac{L}{3^{n-k+1}} = 3^{k-1} \cdot l_1 )</td>
<td></td>
</tr>
<tr>
<td>Fractal dimension: ( D )</td>
<td>( \frac{\ln 20}{\ln 3} = 2.7268 \ldots )</td>
<td>( \frac{\ln 14}{\ln 3} = 2.4022 \ldots )</td>
</tr>
<tr>
<td>Internal surface area: ( S_n )</td>
<td>( 2 \left( 20^n - 8^n \right) \left( \frac{L}{3^n} \right)^2 )</td>
<td>( 6 \left( 14^n - 5^n - 14^{n-1} \right) \left( \frac{L}{3^n} \right)^2 )</td>
</tr>
<tr>
<td>Pore volume: ( V_n )</td>
<td>( \left( 27^n - 20^n \right) \left( \frac{L}{3^n} \right)^3 )</td>
<td>( \left( 27^n - 14^n - 14^{n-1} \right) \left( \frac{L}{3^n} \right)^3 )</td>
</tr>
<tr>
<td>Surface area of ( k^{th} ) pore: ( S_{n,k} )</td>
<td>( 3 \cdot 20^n \left( \frac{8}{20} \right)^k \left( \frac{L}{3^n} \right)^2 )</td>
<td>( 14^n \left( \frac{5}{14} \right)^k \left( \frac{L}{3^n} \right)^2 \cdot \frac{48/5}{54/5} ) if ( k = 1 )</td>
</tr>
<tr>
<td>Volume of ( k^{th} ) pore: ( V_{n,k} )</td>
<td>( \frac{7 \cdot 20^n}{27} \frac{27}{20} \left( \frac{L}{3^n} \right)^3 )</td>
<td>( 14^n \left( \frac{27}{14} \right)^k \left( \frac{L}{3^n} \right)^3 \cdot \frac{12/27}{13/27} ) if ( k = 1 )</td>
</tr>
<tr>
<td>Cohesion boundary ( A_{n,i,j} ) between two pore generations ( i &lt; j )</td>
<td>( 24 \cdot 20^{n-j} \cdot 8^{j-i-1} \cdot 9^{j-1} \left( \frac{L}{3^n} \right)^2 )</td>
<td>( 216 \cdot 14^{n-j} \cdot 5^{j-i-1} \cdot 9^{j-1} \left( \frac{L}{3^n} \right)^2 )</td>
</tr>
<tr>
<td>Total connecting surface area ( A_n )</td>
<td>( \frac{2}{11} \left( 20^n - 12 \cdot 9^n + 11 \cdot 8^n \right) \left( \frac{L}{3^n} \right)^2 )</td>
<td>( \frac{6}{5} \left( 4 \cdot 14^n - 9 \cdot 9^n + 5 \cdot 5^n \right) \left( \frac{L}{3^n} \right)^2 )</td>
</tr>
<tr>
<td>Structure parameter ( \Delta_{n,k} )</td>
<td>( \frac{2}{7} \left( 1 - \left( \frac{2}{5} \right)^{n-k} \right) )</td>
<td>( 24 \cdot \left( 1 - \left( \frac{5}{14} \right)^{n-k} \right) \cdot \frac{1/12}{1/13} ) if ( k = 1 )</td>
</tr>
</tbody>
</table>
Appendix

Appendix II Formulas: adhesion types in the two structures

The tables below contain the number of adsorption sites with different adsorption energies. In contrast to Appendix I, here also the dependence on $m$ must be considered.

1. Total number of sites with given binding energy

Case $m = 1$:

<table>
<thead>
<tr>
<th>Menger-Sponge</th>
<th>Menger-Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a $6 \cdot 20^{-n-1}$</td>
<td>$12 \cdot 14^{-n-1}$</td>
</tr>
<tr>
<td>3a —</td>
<td>$16/91 \cdot (14^n - 14)$</td>
</tr>
<tr>
<td>2a $72/17 \cdot (20^{-n-1} - 3^{-n-1})$</td>
<td>$6/91 \cdot (5 \cdot 14^n - 91 \cdot 2^n + 112)$</td>
</tr>
<tr>
<td>1a $48 \cdot \left(\frac{(20^{-n-1} - 8^{-n-1})}{3} - 3/17 \cdot (20^{-n-1} - 3^{-n-1})\right)$</td>
<td>$3/91 \cdot (29 \cdot 14^n - 182 \cdot 5^n + 364 \cdot 2^n - 224)$</td>
</tr>
</tbody>
</table>

Case $m > 1$:

<table>
<thead>
<tr>
<th>Menger-Sponge</th>
<th>Menger-Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a —</td>
<td>$24 \cdot 14^{-n-1} + 16/91 \cdot (14^n - 14)$</td>
</tr>
<tr>
<td>2a $24/17 \cdot m \cdot (20^n - 3^n)$</td>
<td>$12m \cdot (6 \cdot 14^n - 2^n - 72 \cdot 14^{-n-1} - 96/13 \cdot (14^n - 1))$</td>
</tr>
<tr>
<td>1a $2 \cdot m^2 \cdot (20^n - 8^n) - 48/17 \cdot m \cdot (20^n - 3^n)$</td>
<td>$6m^2 \cdot (14^n - 5^n - 14^{-n-1}) - 12m \cdot (12 \cdot 14^{-n-1} - 2^n) + 96/13 \cdot (14^n - 1) + 72 \cdot 14^{-n-1}$</td>
</tr>
</tbody>
</table>

2. Number of sites with given binding energy in pore generations $k = 1 \ldots n$

Case $k = 1$:

<table>
<thead>
<tr>
<th>Menger-Sponge</th>
<th>Menger-Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a ($m = 1$) $6 \cdot 20^{-n}$</td>
<td>$12 \cdot 14^{-n}$</td>
</tr>
<tr>
<td>3a ($m &gt; 1$) —</td>
<td>$24 \cdot 14^{-n}$</td>
</tr>
<tr>
<td>2a ($m &gt; 1$) $24 \cdot 20^{-n} \cdot m$</td>
<td>$12 \cdot 14^{-n} \cdot (5m - 6)$</td>
</tr>
<tr>
<td>1a ($m &gt; 1$) $24 \cdot 20^{-n} \cdot (m^2 - 2 \cdot m)$</td>
<td>$24 \cdot 14^{-n} \cdot (2m^2 - 5m + 3)$</td>
</tr>
</tbody>
</table>
Case $k > 1$:

<table>
<thead>
<tr>
<th></th>
<th>Menger-Sponge</th>
<th>Menger-Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>—</td>
<td>$32 \cdot 14^{n-k}$</td>
</tr>
<tr>
<td>2a</td>
<td>$24 \cdot 20^{n-k} \cdot 3^{k-1} \cdot m$</td>
<td>$12 \cdot 14^{n-k} \cdot (3 \cdot 2^k \cdot m - 8)$</td>
</tr>
<tr>
<td>1a</td>
<td>$24 \cdot 20^{n-k} \cdot (8^{k-1} m^2 - 2 \cdot 3^{k-1} \cdot m)$</td>
<td>$6 \cdot 14^{n-k} \cdot (9 \cdot 5^{k-1} \cdot m^2 - 24 \cdot 2^{k-1} \cdot m + 16)$</td>
</tr>
</tbody>
</table>
Appendix

Appendix III Small systems

1. Derivation of adsorption isotherms for m=1

As seen in Chapter 2 (Eq. 2.20), the calculation of the adsorption isotherms \( \theta = \theta(y_{re}) \) reduces to that of the partition functions \( Z_{N}^{AD} \). The latter depend on the energy \( E \) (Eq. 2.18) of the given prefractal structure and the applied boundary conditions, which in this case are assumed to be periodic.

The system size of the structures \( MS_1(m) \) and \( MF_1(m) \) with \( m=1 \) is so small (Table 3.1) that one can enumerate by hand all the \( 2^{N_{sat}} \) possible states with \( N=0 \ldots N_{sat}^{AD} \) adsorbed molecules. In addition, the calculations for \( MF_1(m=1) \) can strongly be simplified. In this structure cohesion contacts are only possible due to periodic boundary conditions. The system can be decomposed into three equivalent non-interacting subsystems, each with \( N = 4 \) adsorption sites. Therefore, the isotherm of a single subsystem with \( N_{sat}^{AD} = 4 \) gives the isotherm of the whole system \( MF_1(m=1) \). Introducing:

\[
x = e^{\frac{\alpha}{kT}} \quad \text{and} \quad y = e^{\frac{\gamma}{kT}} \quad (3.17a,b)
\]

the functions \( Z_{N}^{AD} \) turn out to be polynomials in variables \( x \) and \( y \), and these are given in the table below.

<table>
<thead>
<tr>
<th>( MS_1(m=1) )</th>
<th>( MF_1(m=1) ) (subsystem with ( N_{sat}^{AD} = 4 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z_1(x,y) = 1 + 6x^4 )</td>
<td>( Z_1(x,y) = 4x^4 )</td>
</tr>
<tr>
<td>( Z_2(x,y) = 12x^8 + 6x^4y + 3x^8y )</td>
<td>( Z_2(x,y) = 2x^8 + 4x^4y )</td>
</tr>
<tr>
<td>( Z_3(x,y) = 8x^{12} + 12x^{12}y + 12x^8y^2 + 3x^8y^3 )</td>
<td>( Z_3(x,y) = 4x^{12}y^2 )</td>
</tr>
<tr>
<td>( Z_4(x,y) = 12x^{16}y + 3x^{16}y^2 + 8x^{12}y^3 + 12x^{12}y^4 )</td>
<td>( Z_4(x,y) = x^{16}y^4 )</td>
</tr>
<tr>
<td>( Z_5(x,y) = 6x^{20}y^5 + 12x^{16}y^5 + 3x^{16}y^6 )</td>
<td>( Z_5(x,y) = x^{20}y^7 )</td>
</tr>
<tr>
<td>( Z_6(x,y) = x^{24}y^9 )</td>
<td>( Z_6(x,y) = x^{24}y^9 )</td>
</tr>
</tbody>
</table>

Table 3.4 The canonical partition functions for the case \( m = 1 \)
2. Derivation of adsorption isotherms for \( m = 2 \)

For the prefractals with \( m = 2 \) the number of states is of the order of \( 2^{56} \approx 10^{16} \) or higher. To calculate the partition functions \( Z_{AD}^N \) a special computer algorithm has been developed, which is similar to the transfer matrix method [67].

The principle of this method is the following: the original system is decomposed into smaller subsystems for which the density of states can simply be calculated. Due to lateral interactions, however, these smaller systems are not independent: the total energy of the original system decomposed into two subsystems \( A \) and \( B \) is given by:

\[
E = E^A + E^B + E^{AB} \tag{3.18}
\]

where the term \( E^{AB} \) results from the interactions at the contact boundaries of the subsystems, and is a consequence of cohesion interactions only.

The density of states of a single subsystem can be described by a list of quartets \( \{N, N_a, N_c, M(N, N_a, N_c)\} \), where the meaning of each quantity is given below:

- \( N \) denotes, as before, the number of particles \( 0 \leq N \leq N_{\text{sat}} \); 
- \( N_a \) and \( N_c \) denote the number of adhesion and cohesion contacts respectively, such that the total energy of the subsystem is given by: \( E(N_a, N_c) = -(a \cdot N_a + c \cdot N_c) \); 
- \( M(N, N_a, N_c) \) gives the number of realizations of the energy in the form \( E(N_a, N_c) \), given the number \( N \) of adsorbed molecules;

It follows immediately that the values \( M(N, N_a, N_c) \) give the coefficients, while \( N_a \) and \( N_c \) stay for the powers of \( x \) and \( y \) of each term in the canonical partition functions \( Z_{AD}^N \).

The interaction \( E^{AB} \) at the contact boundaries between two subsystems makes the determination of the partition functions of the original systems very difficult since, additionally to the list of quartets \( \{N, N_a, N_c, M(N, N_a, N_c)\} \) of each subsystem, also a fourth parameter \( L \) is needed. The latter describes the state of the subsystems at the contact boundaries and results in a list of quintets \( \{L, N, N_a, N_c, M(L, N_a, N_c)\} \). The density of states of the large system, for each number \( N \) of adsorbed molecules, results from the following composition rules for the number of molecules, of adhesion and cohesion contacts and the multiplicity of the energy respectively:
\[ N = N^A + N^B \]
\[ N^o = N^o_A + N^o_B \]
\[ N^c = N^c_A + N^c_B + N^{cAB} \]
\[ M = M^A \cdot M^B \]  

(3.19)

where the superscripts \( A \) and \( B \) refer to the quantities of the corresponding subsystems.

Using this method, partition functions have been computed in a reasonable time on the Beowulf Computing Cluster of ETH Zürich. Further, adsorption isotherms result directly from the general formula Eq. (2.20). These, however, contain too many terms in order to be reproduced here: the isotherm of \( MS_1(m = 2) \) alone would fill about 70 A4 pages. The formulas are stored in Mathematica Notebook files and this program is used also for the representation of the adsorption isotherms. Here only the partition functions \( Z_{1D}^2(x,y) \) and \( Z_{2D}^2(x,y) \) are reproduced:

\[ MS_1(m = 2): \]
\[ Z_{1D}^2(x,y) = 8 + 48x^2 \]
\[ Z_{2D}^2(x,y) = 84x^4y + 24x^2y^2 + 12y + 1044x^4 + 360x^2 + 16 \]  

\[ MF_1(m = 2): \]
\[ Z_{1D}^2(x,y) = 8x + 16x^2 + 8x^3 \]  
\[ Z_{2D}^2(x,y) = 16x^2 + 112x^3 + 168x^4 + 112x^5 + 24x^6 + 12x^2y + 16x^3y + 16x^4y + 16x^5y + 4x^6y \]  

(3.20)

(3.21)
3. The first and second derivatives of $\theta$ according to the relative fugacity at $\gamma_{rel} = \lambda = 0$

Below the formulas for the first and second derivatives according to $\gamma_{rel}$ at $\gamma_{rel} = \lambda = 0$ are given. The second derivative is used for the determination of the transition from convex to concave behavior in section 3.3.2.

General formulas:

$$\theta' (0) = \frac{Z_1 (x, y)}{N_{AD, sat} \cdot y}$$

$$\theta'' (0) = \frac{2 \left( 2 Z_2 (x, y) - Z_1^2 (x, y) \right)}{N_{AD, sat} \cdot y^3}$$

Formulas (3.22) applied for each structure:

**$MS_1 (m=1)$**:

$$\theta' (0) = \frac{1 + 6 x^4}{7 y^3}$$

$$\theta'' (0) = \frac{2 \left( 6 x^4 (y - 2) + 12 x^4 (y - 1) - 1 \right)}{7 y^6}$$

**$MF_1 (m=1)$**:

$$\theta' (0) = \frac{x^4}{y^3}$$

$$\theta'' (0) = \frac{2 x^8 (2 y - 3)}{y^6}$$

**$MS_1 (m=2)$**:

$$\theta' (0) = \frac{1 + 6 x^2}{7 y^3}$$

$$\theta'' (0) = \frac{2 \left( 3 x^4 (7 y - 9) + 6 x^2 (y - 1) + 3 y - 4 \right)}{7 y^6}$$

**$MF_1 (m=2)$**:

$$\theta' (0) = \frac{x + 2 x^2 + x^3}{4 y^3}$$

$$\theta'' (0) = \frac{x^3 (1 + x^2) \left( x^2 (y - 2) + 4 x (y - 1) + 3 y - 4 \right)}{2 y^6}$$
Appendix

4. Expression for the isotherms in the absence of lateral interactions (c=0)

\( M_S_1 (m = 1): \)

\[
\theta (\gamma_{rel}) = \frac{1}{7} \cdot \frac{\gamma_{rel}}{1 + \gamma_{rel}} + \frac{6}{7} \cdot \frac{x^3 \gamma_{rel}}{1 + x^3 \gamma_{rel}}
\]  
(3.27)

\( M_F_1 (m = 1): \)

\[
\theta (\gamma_{rel}) = \frac{x^4 \gamma_{rel}}{1 + x^4 \gamma_{rel}}
\]  
(3.28)

\( M_S_1 (m = 2): \)

\[
\theta (\gamma_{rel}) = \frac{8}{56} \cdot \frac{\gamma_{rel}}{1 + \gamma_{rel}} + \frac{48}{56} \cdot \frac{x^2 \gamma_{rel}}{1 + x^2 \gamma_{rel}}
\]  
(3.29)

\( M_F_1 (m = 2): \)

\[
\theta (\gamma_{rel}) = \frac{8}{32} \cdot \frac{x \gamma_{rel}}{1 + x \gamma_{rel}} + \frac{16}{32} \cdot \frac{x^2 \gamma_{rel}}{1 + x^2 \gamma_{rel}} + \frac{8}{32} \cdot \frac{x^3 \gamma_{rel}}{1 + x^3 \gamma_{rel}}
\]  
(3.30)
5. Adsorption isotherms of the four structures

On the following page the isotherms of the four small structures are reproduced as an illustration of the critical adhesion to cohesion ratio \( a/c = 0.5 \). In order to emphasize the differences between the Sponge and the Filter, the isotherms for the same \( m \) value are shown side by side with solid and dashed lines for the two structures respectively. On each picture the arrows point towards the direction of decreasing temperature (increasing \( c/kT \)), the isotherms correspond to the values \( c/kT = 1.5, 2 \) and 3 respectively.
<table>
<thead>
<tr>
<th>$a/c=0.7 &gt; 0.5$</th>
<th>$a/c=0.5$</th>
<th>$a/c=0.4 &lt; 0.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS($m=2$) solid line and MF($m=2$) dashed line</td>
<td>MS($m=1$) solid line and MF($m=1$) dashed line</td>
<td>Model Limit</td>
</tr>
</tbody>
</table>
6. Determination of the critical value of \( a/c \) and of the limit isotherms for \( T \to 0 \)

In order to determine the critical adhesion to cohesion ratio, the adsorption isotherm (2.20) is brought to the form:

\[
\theta = \frac{1}{N_{\text{sat}}^{\text{AD}}} \sum_{N=1}^{N_{\text{AD}}} N \cdot Z_N^{\text{AD}} \cdot y^{y(N_{\text{AD}} - N)} \gamma_{\text{rel}}^N \left( y^{y(N_{\text{AD}}) + \sum_{N=1}^{N_{\text{AD}}} Z_N^{\text{AD}} \cdot y^{y(N_{\text{AD}} - N)} \gamma_{\text{rel}}^N} \right) \tag{3.31}
\]

Both the numerator and the denominator in the above expression are polynomials of \( x \) and \( y \). The limit isotherm for \( T \to 0 \) (\( x \to \infty, y \to \infty \)) can be found by locating the terms with largest exponents. At this stage, two observations can be made:

1. All terms are built up from mixed powers of \( x \) and \( y \); thus the dominating terms depend finally on the adhesion to cohesion ratio. In this sense it is useful to introduce the new variable \( z = e^{1/kT} \) and to note that in this case:

\[
x = za, \quad y = z^c \quad \text{and} \quad y^{yN_{\text{AD}}} = z^{3yN_{\text{AD}}} \tag{3.32}
\]

2. Corresponding terms of the two sums found in the denominator and the numerator of Eq. (3.31), i.e. without considering the term \( y^{yN_{\text{AD}}} \), contain the same powers of \( x \) and \( y \); therefore, the final result will be determined by \( y^{yN_{\text{AD}}} \) and the dominant terms of the two sums.

Keeping this in mind, the following three cases may be distinguished:

L1. If the term \( y^{yN_{\text{AD}}} \) dominates then the limit isotherm is zero for all \( \gamma_{\text{rel}} \).

L2. If the terms, which dominate in both sums, are of the same order as \( y^{yN_{\text{AD}}} \), then \( \theta \) is a non-constant continuous function of \( \gamma_{\text{rel}} \); it is determined by the coefficients of the largest terms, which contain powers of \( \gamma_{\text{rel}} \).

L3. If the dominating terms in both sums are of a higher order than \( y^{yN_{\text{AD}}} \), then the limit isotherm is determined by their coefficients.

It will be proven that the three cases described above correspond exactly to \( a/c < 0.5 \), \( a/c = 0.5 \) and \( a/c > 0.5 \) respectively. The proof is based on the following three results:
Appendix

**Result 1.** At saturation, the following relation holds between the saturation number $N_{\text{sat}}^{AD}$ and the number $N_{a,\text{sat}}$ and $N_{c,\text{sat}}$ of adhesion and cohesion contacts at saturation, respectively:

$$N_{a,\text{sat}} + 2 \cdot N_{c,\text{sat}} = 6 \cdot N_{\text{sat}}^{AD} \quad (3.33)$$

**Proof:** The $N_{\text{sat}}^{AD}$ molecules at saturation can take part in a total of $6 \cdot N_{\text{sat}}^{AD}$ pair interactions. From these a number of $N_{a,\text{sat}}$ come from the interaction with the solid material. Further there are a total of $N_{c,\text{sat}}$ pair interactions between adsorbed molecules, but the latter are counted twice in $6 \cdot N_{\text{sat}}^{AD}$. Due to periodic boundary conditions, there are no further contributions to the total number of pair interactions at saturation.

**Result 2.** Consider a state $A$ with $N^A$ adsorbed molecules, $N_{c}^{A}$ cohesion interactions and $N_{a}^{A}$ adhesion interactions such that $1 \leq N^A < N_{\text{sat}}^{AD}$. Further, let $N^{\text{gat}}_{\text{ad}}$ denote the number of bonds on the lattice, for which the two endpoints correspond to an adsorbed molecule and an unoccupied adsorption site respectively (this may also be thought of as the number of unsaturated bonds of adsorbed molecules of the state $A$). Then we have the following relation:

$$N_{a}^{A} + 2 \cdot N_{c}^{A} + N^{\text{gat}}_{\text{ad}} = 6 \cdot N^A \quad (3.34)$$

**Proof:** The proof follows directly from relation (3.33). It is important to note that when $1 \leq N^A < N_{\text{sat}}^{AD}$ and the pore space is interconnected (i.e. the size $\overline{N}$ of the largest connected cluster of adsorbed molecules at saturation equals $N_{\text{sat}}^{AD}$), one always has: $N^{\text{gat}}_{\text{ad}} > 0$. The first generation Menger-Filter is an exception, since there the pore space is not interconnected. The present results, however, can also be applied for the Menger-Filter by replacing $N_{\text{sat}}^{AD}$ with $\overline{N}$. (see also the explanation in section 1 of Appendix III)

**Result 3.** If $a/c \geq 0.5$, and the pore space is interconnected, then the dominating term in the sums of the numerator and denominator of the isotherm (3.31) is provided by the fully saturated state.
Appendix

Proof: The term \( T_{\text{sat}}(x, y) \) corresponding to the saturated state is given by:

\[
T_{\text{sat}}(x, y) = x^{N_{a,\text{sat}}} \cdot y^{N_{c,\text{sat}}} = z^{aN_{a,\text{sat}}+cN_{c,\text{sat}}}
\]  

(3.35)

Any other term \( T(x, y) \) in these sums corresponds to a state \( A \) with \( 1 \leq N < N_{\text{sat}}^{AD} \) adsorbed molecules, \( N_{c}^{A} \) cohesion interactions and \( N_{o}^{A} \) adhesion interactions such that:

\[
T(x, y) = x^{N_{a}} \cdot y^{N_{c}} \cdot y^{3 \left( N_{\text{sat}}^{AD} - N \right)} = z^{aN_{a}+cN_{c}+3c \left( N_{\text{sat}}^{AD} - N \right)}
\]  

(3.36)

The dominance of the term \( T_{\text{sat}}(x, y) \) over the other terms \( T(x, y) \) is equivalent to:

\[
a \cdot N_{a,\text{sat}} + c \cdot N_{c,\text{sat}} > a \cdot N_{a}^{A} + c \cdot N_{c}^{A} + 3c \cdot \left( N_{\text{sat}}^{AD} - N^{A} \right)
\]  

(3.37)

or:

\[
a \cdot \left( N_{a,\text{sat}} - N_{a}^{A} \right) + c \cdot \left( N_{c,\text{sat}} - N_{c}^{A} \right) > 3c \cdot \left( N_{\text{sat}}^{AD} - N^{A} \right)
\]  

(3.38)

One considers the complementary state \( B \) of \( A \), which is obtained by inverting the “lattice spins”. For this new state \( B \) the following relations hold:

\[
N_{\text{sat}}^{AD} - N^{A} = N^{B}
\]

\[
N_{a,\text{sat}} - N_{a}^{A} = N_{a}^{B}
\]

\[
N_{c,\text{sat}} - N_{c}^{A} = N_{c}^{B} + N_{c}^{\text{BB}}
\]  

(3.39)

where, as in Result 2., \( N_{c}^{\text{BB}} \) stays for the number of unsaturated bonds of the adsorbed molecules of the state \( B \).

Proving inequality (3.38) therefore reduces to show that:

\[
a \cdot N_{a}^{B} + c \cdot \left( N_{c}^{B} + N_{c}^{\text{BB}} \right) > 3c \cdot N^{B}
\]  

(3.40)

Applying relation (3.34) to the state \( B \) and dividing both sides with \( c \) one obtains:
Appendix

\[ \alpha / c \cdot N^B_a + N^B_c + N^BB > 0.5 \cdot N^B_a + N^B_c + 0.5 \cdot N^BB \]  \hspace{1cm} (3.41)

The strict inequality (3.41) follows from the conditions \( \alpha / c \geq 0.5 \) and \( N^BB > 0 \), where the latter inequality is strict for \( N^B < N^{AD}_{sat} \) and \( \overline{N} = N^{AD}_{sat} \). This proves the Result 3.

**Application of the results 1 -3**

**Case L2.** Applied to \( \alpha / c = 0.5 \), Result 1. states exactly \( z^{a N^A_{sat} + c N^A_{sat}} \) and \( y^{N^{AD}_{sat}} = z^{c N^{AD}_{sat}} \) to be of the same order. Result 3. then gives the dominating terms in the isotherm (highlighted below) and leads to the limit isotherm:

\[ \theta = \lim_{z \to 0} \frac{1}{N^{AD}_{sat}} \left( \frac{... + N^{AD}_{sat} \cdot z^{a N^A_{sat} + c N^A_{sat}} \cdot y^{N^{AD}_{rel}}}{z^{3c N^{AD}_{sat}} + ... + z^{a N^A_{sat} + c N^A_{sat}} \cdot y^{N^{AD}_{rel}}} \right) = \frac{y^{N^{AD}_{rel}}}{1 + y^{N^{AD}_{rel}}} \]  \hspace{1cm} (3.42)

As explained previously under Result 2., the exponent \( N^{AD}_{sat} \) in isotherm (3.42) is correct only when the pore space is totally interconnected, i.e. if \( \overline{N} = N^{AD}_{sat} \). When \( \overline{N} < N^{AD}_{sat} \), (e.g. Menger Filter for \( n = 1 \)), the isotherm (3.42) turns into:

\[ \theta = \frac{y^{N}_{rel}}{1 + y^{N}_{rel}} \]  \hspace{1cm} (3.43)

**Case L3.** Following the same reasoning as for L2 on finds that for \( \alpha / c > 0.5 \) the largest terms in the sums dominate the term \( y^{N^{AD}_{sat}} = z^{c N^{AD}_{sat}} \) and this leads to:

\[ \theta = \lim_{z \to 0} \frac{1}{N^{AD}_{sat}} \left( \frac{... + N^{AD}_{sat} \cdot z^{a N^A_{sat} + c N^A_{sat}} \cdot y^{N^{AD}_{rel}}}{z^{3c N^{AD}_{sat}} + ... + z^{a N^A_{sat} + c N^A_{sat}} \cdot y^{N^{AD}_{rel}}} \right) = \begin{cases} 0 & \text{for } y^{N}_{rel} = 0 \\ 1 & \text{for } y^{N}_{rel} > 0 \end{cases} \]  \hspace{1cm} (3.44)

i.e. the degenerated form of the Type I isotherm in the IUPAC classification.
Case L1. It will be shown that for \( a/c < 0.5 \) the term \( y^{3c-N_{sat}^{AD}} = z^{3c-N_{sat}^{AD}} \) dominates all other terms \( T(x,y) \) in the sums of the isotherm (3.31), i.e.:

\[
3c \cdot N_{sat}^{AD} > a \cdot N_a + c \cdot N_c + 3c \cdot (N_{sat}^{AD} - N)
\]

(3.45)

or equivalently:

\[
3c \cdot N > a \cdot N_a + c \cdot N_c
\]

(3.46)

where \( N_a \) and \( N_c \) are the number of adhesion and cohesion pair interactions respectively of a state with \( N \) adsorbed molecules, where \( 1 \leq N \leq N_{sat}^{AD} \). Substituting relation (3.34) into the inequality (3.46) one finds that:

\[
c / 2 \cdot N_a + c \cdot N_c + c \cdot N^0 > a \cdot N_a + c \cdot N_c
\]

(3.47)

The condition \( a/c < 0.5 \) assures for a strict inequality in (3.47) and therefore, the limit isotherm, highlighting only the dominant term, is given by:

\[
\theta = \lim_{z \to \infty} \frac{1}{N_{sat}^{AD}} \left( z^{N_{sat}^{AD} - a \cdot N_{sat}^{AD} \cdot N_{sat}^{AD} \cdot N_{sat}^{AD}} \right) = 0
\]

(3.48)

This closes the proofs needed for the critical adhesion to cohesion ratio.
Appendix

Appendix IV Large systems: technical details related to Grand Canonical Monte Carlo simulations

Adsorption isotherms of the prefractal structures were calculated using a Metropolis spin flip algorithm implemented in C++. Calculations were performed on the Beowulf computing cluster of ETH Zürich. The computer memory size imposed a maximum of about 1.2 million lattice points which could be handled in a simulation. In this way prefractal structures up to the fourth generation have been studied, comprising a self-similarity extended over two orders of magnitude. This range includes the micropores and the lower part of the mesopores which is completely satisfactory from the point of view of the present study.

Adsorption isotherms were constructed by calculating the adsorbed amount at 120 equidistant points of relative pressures in the range \( p/p_0 = 0 \) to \( p/p_0 = 1 \). Depending on the systems size, the number of total spin-updates performed at each relative pressure varied between 5000 for the larger systems of several hundred thousand lattice points up to 40000 for the systems of the order of several thousand molecules. At each simulation the first half of the total updates have been used to attain equilibrium (thermalization) while the adsorbed amount has been calculated as the average taken over the second half of simulated states.

The last simulated state at the relative pressure \( p_k \) served as the initial state for the simulation at the relative pressure \( p_{k+1} \) such that until the end the number of executed spin updates have been cumulated. This had an importance especially at pressures close to the saturation since here many more spin updates are necessary to attain equilibrium. Beside the total adsorbed amount in the prefractals several other quantities like the adsorbed amount in each pore generation, for each adhesion type and also at each adhesion type in any pore generation has been determined. These partial isotherms (Eqs. 2.23-24) have been used to obtain a complete picture about the various adsorption mechanisms in the prefractals.
Appendix V Experimental isotherms from the literature

**Fig V.1 a)** The IUPAC classification of adsorption isotherms [1]; **b)** stepwise isotherms of water found on silica [62].

**Fig V.2 a)** Stepwise isotherms of water on silica [56]; **b)** Dependence of water adsorption in hydrated Portland cement on temperature [63].
Appendix

**Fig V.3** Adsorption isotherms of water on oxygenated carbon heated previously to temperatures between 200°C – 1150°C; this affected the water affinity of the surface and resulted in different isotherms ([1] page 263.)
References

References


Curriculum Vitae

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2002-2006  Doctorate study at the Chair of Building Physics, ETH Zurich: “Moisture Adsorption on 3D Self-Similar Structures”
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