



## The confinement effect in zeolites

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### ARTICLE INFO

*Article history:*  
Available online 6 November 2008

*Keywords:*  
Confinement  
Zeolites  
Catalysis  
Theory  
Orbitals

### ABSTRACT

As microporous materials, zeolites entrap molecules allowing their diffusion, adsorption and reaction within the channel system. This confinement affects the physico-chemistry of such incoming molecules in different ways. Derouane pioneered research onto the confinement effect in zeolites and extracted ideas and conclusions regarding physisorption, catalytic cracking and diffusion. His work on this topic is reviewed in this article and further updates on the confinement effects by other groups are also analysed.

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### 1. Introduction

Catalysis is a very interdisciplinary field, which encompasses concepts and contributions from all chemistry areas. In particular, scientists working on catalysis with a solid footage on physical chemistry are good candidates to permeate and enrich both areas of chemistry and such is the case of Professor Eric G. Derouane to whom this contribution is dedicated. His main fields of investigation dealt with catalysis over zeolites, supported metals, mixed oxides, fine chemicals, superconductors, combinatorial catalysis and high throughput technology, asymmetric catalytic hydrogenation, enzyme mimetics, and Friedel–Crafts reactions amongst others [1].

A particularly important concept that we would like to highlight here was widely elaborated by Derouane and it is related to the confinement effect of zeolites on adsorbing/diffusing molecules throughout its micropore environment. In fact, every introductory course on zeolites readily highlights the confinement as the most ubiquitous and intriguing fingerprint of zeolites, whose effect is at the same time essential and difficult to quantify. Apart from Derouane's contributions – which we analyse here – few studies, if any, have been addressed to attempt a fundamental understanding of the confinement effect in zeolites [2–5].

Apart from their chemical nature as alumino-silicates and related materials, zeolites have remarkable properties resulting from the surface curvature of their internal surface. This results in non-covalent interactions between the zeolite framework and

molecules located in their intracrystalline free space [6]. These interactions are repulsive (Pauli repulsion type of interactions) in the short range and attractive (van der Waals type of interactions) in the long range. Effects related to these interactions are shape selectivity, selective adsorption, and enhanced diffusivity. Confinement effects make zeolites behave as solid solvents and some consequences of it can be treated in analogy to solvent effects.

The description of zeolites as solid solvents was first introduced in 1979 by Barthomeuf [7] who pointed out the effect of the electric field gradient (due to the aluminum and cation distribution) on the alkane reactivity. According to this, under the influence of such field gradients, molecules will be polarized to different extents depending on the cage type, with the appearance of induced dipoles and multipoles, weakening or strengthening some C–C bonds. This, in turn, leads to cracking mechanisms different from the classical  $\beta$ -scission based on the stability of carbenium ions in a non-disturbing environment. Mechanisms similar to those of superacids in solution, involving a pentacoordinated carbonium ion are then possible in zeolites [8,9]. Part of the work by Barthomeuf related to the electric field gradient in zeolites was particularly implicit in the early study of electrostatic fields in zeolites by Dempsey in 1969 [10–13], although in none of these studies by Dempsey and Barthomeuf appears yet an explicit treatment on how incoming molecules are disturbed when entering the zeolite pores, taking into account zeolite-molecule (host-guest) interactions.

Kiselev did explicitly mention the nature of the host-guest interactions between adsorbed molecules in zeolites in an early and inspiring contribution made in 1965 [14]. In later work, which he pioneered by applying atomistic molecular dynamics to

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zeolites in 1981 did not explicitly mention effects of confinement on the adsorption energies of several substrates over zeolites [15].

## 2. The nest effect

In 1986, Derouane made a seminal contribution and introduced what he called the ‘nest effect’ to suggest that the activity and selectivity of different zeolites in cracking of n-pentane could be related to the zeolitic pore size [2], showing that diffusional limitations imposed on the products and/or the reactants, as well as structural constraints acting on reaction intermediates or transition state(s), and channel differentiation (size and shape) could be determining. Derouane argued using the concept of surface curvature, introduced by Andersson et al. [16,17], that van der Waals interactions are proportional to the curvature of periodic minimal Gaussian surfaces, and that this concept could be used to discuss water sorption and hydrocarbon cracking by zeolites. The nest effect tends to optimise such van der Waals interactions and it involves a perturbation on the shape and electronic structure of the sorbed species leading to sorbate-induced framework structural changes. This enables molecules to reach minimum energy points on the sorbate-zeolite van der Waals potential surface, thus increasing the sorption equilibrium constant and the local concentration of the chemical species (reactants, intermediates, and transition state complexes) involved, which in turn affects reaction kinetics, activity and selectivity [2]. Sorption will be favored for the species, which have the best ability to “nest” within the zeolite channels and this will depend on the relative match between the molecules and the pore (cavity) sizes, shapes, and lengths. For a given type of molecular species, there should be an optimum sorption pore size (and shape), which will favor its catalytic conversion, and this effect can act separately or in addition to acid strength. Plotting Turnover frequencies for n-pentane cracking on several zeolites versus pore size, Derouane was able to show a “volcano-type” plot indicating the existence of an optimal pore diameter equal to about 5.8–6.0 Å, which is close to that of linear paraffins [2].

Similar ideas, under the name ‘inverse shape selectivity’, were later used by Santilli et al. [18] to explain the results of C6 cracking in zeolites with different pore sizes. The authors found that zeolites with pores within the range 7.0–7.4 Å selectively adsorb and, during cracking reactions, produce branched C6 alkanes. The selectivity for adsorbing branched alkanes over linear ones was explained by attractive forces between the zeolite walls and the adsorbed hydrocarbons. During hydrocracking reactions catalyzed by these zeolites, it was found that stabilizing interactions between the walls and the methyl-branched transition states lead to the selective formation of branched products. This preference for adsorbing or producing branched hydrocarbons was called “inverse shape selectivity”. Modelling of competitive adsorption of hydrocarbons with Monte Carlo methods showed inverse shape selectivity in zeolite structures with 6.5–7.3 Å pores and predicted that inverse shape selectivity could be found in pores up to 8 Å in diameter but not in pores larger than 9 Å. Along similar grounds, Corma et al. [19] explained results of n-heptane catalytic cracking in different zeolites based on the different pore size architecture.

Zeolites though, contain normally an heterogeneous pore system, which makes difficult to assign a unique pore size descriptor to a given structure and in this sense, the more elaborated concept of ‘constraint index’, based on the original ideas introduced by Haag et al. [20] in 1991, was later organised and developed by Zones and Harris [21] and Macedonia and Maginn [22].

## 3. The confinement effect

One year later than the paper on the nest effect [2], Derouane et al. published three important contributions [3–5], which provided a theoretical basis for what was then called the confinement effect. The latest of these, written in 1988 [5], is Derouane’s most cited paper and this speaks about the importance that this concept received in the scientific community. In these papers the following equation was proposed for the van der Waals energy ( $W$ ) of a spherical molecule of a certain van der Waals radius ( $d$ ) confined in a micropore of a given radius ( $a$ ):

$$W = \frac{-C}{4d^3 \left(1 - \frac{s}{2}\right)^3}$$

where  $s = d/a$  is a parameter that can vary between the values 0 and 1, depending on the relative size of the confined molecule and the micropore. The extreme cases correspond to a flat surface ( $s = 0$ ) and to a molecule with the same size than the pore ( $s = 1$ ), the latter being called by Derouane and coworkers a ‘floating molecule’. It easily follows that and this means that, according to  $W_{(s=1)} = 8W_{(s=0)}$  this model, the adsorption energy due to van der Waals confinement factors within the zeolite pore can be up to 8 times larger than that corresponding to a flat surface. The type of variation of  $W$  versus  $s$  can be found in Fig. 1.

Also an equation was derived for the force acting over the molecule as follows:

$$F = \frac{3C}{4d^4} \frac{1-s}{\left(1 - \frac{s}{2}\right)^4}$$

whose corresponding plot is shown in Fig. 2, from which follows that at  $s = 1$ , the force is equal to zero and hence the particle achieves a state of supermobility. Derouane and coworkers obtained interesting consequences regarding the supermobility of ‘floating’ molecules in zeolites, a state in which the van der Waals attraction (which causes adsorption) is cancelled out by an equal and opposite repulsive force.

### 3.1. Confinement and physisorption

One consequence of confinement regards physisorption of molecules in zeolites. The confinement effect can explain why sometimes heats of sorption at low coverage are larger than at

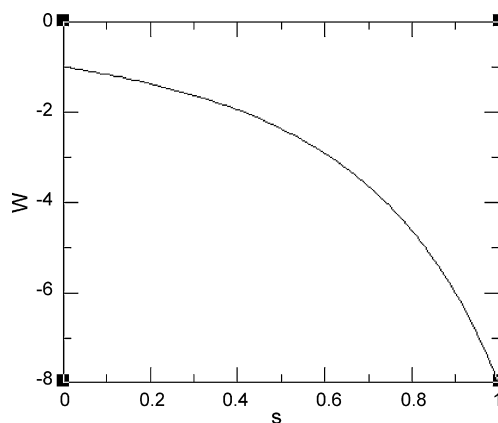
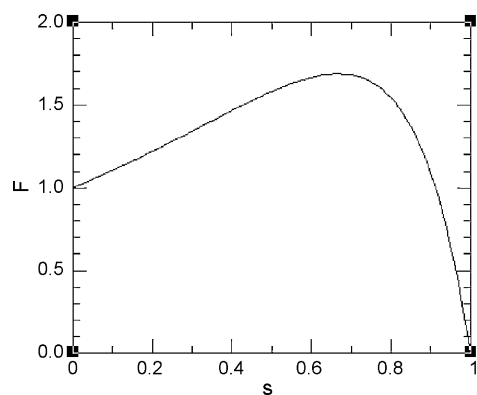


Fig. 1. Variation of the van der Waals energy between a spherical molecule (radius  $d$ ) and a spherical micropore (radius  $a$ ) with the  $s = d/a$  parameter.  $s = 0$  corresponds to a flat surface, whilst  $s = 1$  corresponds to a sorbate matching the pore size. Values of  $W$  are relative to the flat surface case.



**Fig. 2.** Variation of the force between a spherical molecule (radius  $d$ ) and a spherical micropore (radius  $a$ ) with the  $s = d/a$  parameter.

higher coverages. Sorbed molecules will first achieve the best possible fit between their size (and shape) and that of the intracrystalline environment in order to maximize their van der Waals attraction energy. For small molecules, higher “zero coverage” (initial) sorption heats will thus be observed as those will be accommodated first in the smallest pores (rings, prisms, side pockets, and channels) where optimal match is achieved, and the sorption heat will rapidly decrease to a plateau for higher coverages. This phenomenon explains the apparent physical site heterogeneity observed in the initial stages of their physisorption. For large and bulky molecules, such a situation occurs only to a very limited extent, which explains the notable absence of this phenomenon in that case. The influence of pore size in physisorption was experimentally confirmed in our group [23], through experiments that made clear the two different aspects of the chemical composition and the pore size, and their influence in the adsorption energies of hexane, and aromatic hydrocarbons in zeolites such as ZSM-11, ZSM-12, SSZ-24 and CIT-1. Microcalorimetric experiments showed the evolution of the differential heat of adsorption with loading from which effects derived of interaction with the micropore surface and the volumetric capacity were both measured. Two behaviours were characterised depending on whether the hydrocarbon molecules adsorbed or not on specific centres. In what confinement effects is concerned, it was established that hexane did not show specific site adsorption, thus mimicking the kind of interaction described by Derouane in the references [3–5], and within this conditions we showed that the heat of adsorption was directly related to the pore size [23].

The confinement can also help to explain barriers posed by external surfaces to sorption. Molecular transfer from the gas into the restricted zeolite channels is unlikely to occur by direct impingement because the molecules will not have the proper orientation relative to the pores. Therefore, their initial physisorption state is likely to be on the zeolite external surface, where the entropy decrease due to adsorption will take place. The diffusion into the intracrystalline void volume occurs by moving over the rim of the pore, which requires an activation energy. Finally, Derouane also suggested [5] that sorbate-induced framework structural changes, as found by Fyfe et al. [24] and by Klinowski et al. [25], could be explained as another consequence of surface curvature.

### 3.2. Confinement and diffusion

Another remarkable result, sometimes perhaps overlooked in the literature, is that the diffusion in zeolites generally obeys what

Derouane called ‘creep motion’ [3,5]: each atom of the diffusing molecule tries to find positions whose distance to the pore wall satisfies the minimum van der Waals energy possible. Only when a significant number of atoms simultaneously happen to get an energy minimum towards a certain micropore region, a collective short jump occurs and the molecule translates through the micropore following the creep motion. This is a qualitative and important feature of diffusion in zeolites rather followed at low temperatures and by large molecules, which was made prior to the computational studies of diffusion of hydrocarbons in zeolites started shortly afterwards Derouane’s comments. One of such early molecular dynamics studies by Theodorou et al. [26] dealt with the mobility of butane and hexane in silicalite, and they found a similar feature than that described previously by Derouane, which the authors called ‘rattling motion’ [26].

The confinement model also allowed to rationalise diffusional mass transfer results of hydrocarbons (n-hexane, 2-methylpentane and 3-methyl-pentane) in zeolites (BEA, MFI, MOR, FAU and AEL) according to the size and shape of their pores and channels showing that an increase of the sticking force ( $F$ , as in Fig. 2) slows transport diffusion [27].

A concept related to diffusional supermobility was developed by Derouane [2–5], which occurs when attractive and repulsive forces between the zeolite and the diffusing molecule cancel out. This is the case when the size of the sorbate almost matches the size of the channel and at this point the micropore channel becomes a guide for the direction of the diffusion where the probability of motions perpendicular to the channel direction becomes negligible. The latter is a very important point, which we would like to explain further. Diffusing molecules are made of atoms and each atom interacts independently and differently within the zeolite channel, this resulting into a speed vector for each diffusing atom as a function of time. In general it is more probable that speed vectors point to different directions and the overall result is the molecular motion. This is not the case of the floating molecule, where the interaction forces cancel out perpendicularly to the channel direction (floating molecule) leaving only the contributions through the channel direction. Thus the atomic velocity vectors point in the channel direction and the result is a much larger molecular motion, which contributes very largely to the diffusivity. After Derouane, this effect was beautifully described by Yashonath and Santikary [28] who found a sharp increase in the (intercage) diffusivity of zeolite Y when the cross-section of the diffusing particle approached the size of the zeolite window. Using Lennard–Jones type of interactions, this effect was shown to be present in all cases where the molecular size approached the channel size, and hence this effect is not linked to either a particular type of zeolite or sorbate. According to this, a guest inside a zeolite cage goes out of the cage through a narrow window located on the sphere. Such a passage through the window or neck is found to be associated with a higher energy barrier if the guest is significantly smaller than the window diameter. If the guest is similar to the window size, then it encounters little or no energetic barrier and it goes past the cage without difficulty. It was also shown that this effect is also present at all ranges of sorbate concentrations and this can be applied for separation purposes. This effect was very appropriately described and studied in depth by Yashonath and Rajappa as a state of levitation [29–31].

### 3.3. Confinement and catalysis

Another remarkable achievement in this paper [5] was that Derouane was able to calculate TOF (turnover frequencies) of n-pentane cracking in different zeolites with incredible accuracy using his confinement model and assuming that all acid sites are

equally strong. The TOF was related to the heats of sorption and they in turn were related to the van der Waals expression, and the following equation was proposed:

$$\lg \text{TOF} = -1.4 + 4.25(R - 1) \quad \text{with } R = \left[ \frac{a(2a_x - d)}{a_x(2a - d)} \right]^2$$

where 'a' and 'd' have the same meaning as in previous equations, and the subscript 'x' refers to a catalyst of reference.

The agreement between calculated and experimental TOFs shows that differences in activity between zeolites are mainly due to adsorption phenomena linked to the confinement effects. Acid strength, according to this interpretation, becomes a secondary argument to explain the catalytic results.

#### 4. Updates in the concept and applications of the confinement effect

The wealth of concepts spread out from these studies [3–5] pervades a considerable part of today's zeolite science and some of the original problems are still subject of much debate as we outline in what follows. Thus, we will now consider the following topics: (i) quantum effects of the confinement, (ii) diffusion of floating molecules, and (iii) van der Waals effect in the synthesis of zeolites.

##### 4.1. Quantum effects of the confinement

As described before, Derouane discussed [2–5] an effect that originates from the interaction of a particle with a curved surface. This is a classical effect due to the specific geometry of the curvature, which provides a different arrangement of interacting atoms than that of a flat surface. More recently [32–36], the confinement effect was approached from a different perspective. The starting point is the consideration that, in general, molecular orbitals span over an unlimited region of the space, but when a confining surface appears the limited boundary implies an increase of the orbital energies. Mathematically, the confinement means a new Hamiltonian with an infinite energy for the system beyond the boundary limits, and whose functional form depends on how abruptly the energy increases as the confined entity approaches such boundary. The new wave function, and its corresponding eigenvalues give the information on the confined system, where in all cases an energy increase of the molecular orbital energies is observed with respect to the unconfined system. This model was introduced by Zicovich-Wilson et al. [32], where the simple case of the hydrogen atom confined in a potential well was studied and the energy of the orbitals was calculated and shown to be higher than that of the unperturbed system. The effects of the confinement were calculated on the ethylene molecular pi-orbitals confined as a function of the pore size [33,34]. Also the effects of changing pore size in Beta, ZSM-5 and ZSM-12 zeolites on the frontier molecular orbitals of benzene were calculated [35] showing an increasing effect as the pore size decreases (the 's' parameter approaches to unity). From the experimental viewpoint a confirmation of the confinement effect on the orbital energies was found in our group [36], where it was shown that the photophysical properties of naphthalene within pure silica zeolites (ferrierite, ZSM-48 and SSZ-24) are strongly affected by the zeolite in which this molecule is confined. Shifts to lower vibration energy of the Raman peaks were found and explained due to the weakening of the naphthalene bonds. The calculated electronic structure of naphthalene within the different zeolites agreed with the experimental observations and indicated that the naphthalene pi-electrons are affected by the confinement effect.

##### 4.2. van der Waals effects in the synthesis of zeolites

This is a point not explicitly mentioned by Derouane, but nevertheless one can consider that if van der Waals interactions can be responsible for an up to eightfold increase in the heat of sorption with respect to a flat surface (see Fig. 1), the same can be said about the organic templates used in the synthesis of zeolites, which act exactly as a physisorbed sorbate molecule. In fact, by definition, template molecules are of similar size to the micropore and hence this means  $s \sim 1$ , where the effects of increasing heats of sorption are more evident.

Organic templates, also called structure directing agents (SDA), started to be of general use in the synthesis of zeolites in the sixties when researchers such as Barrer [37] and Kerr [38], started to look for suitable molecules designed for each particular micropore shape and size. It was thought that the organic molecule shaped the silica polymerisation reactions, allowing the crystalline phase to be obtained if the final system provided that the 'zeolite + organic-occluded' system has a sufficiently favourable energy. This sufficiently favourable energy can be achieved by a close contact between the atoms of the organic template and the atoms of the zeolite micropore and hence this is more easily achieved when the 's' parameter is close to unity.

Later, three contributions made between 1989 and 1992 by Zones [39], Gies and Marler [40], and Davis and Lobo [41], rank amongst the first studies that helped to rationalise how organic templates lowered the energy of the system zeolite + SDA, where the role of the van der Waals interactions is explicitly mentioned. Proper computational studies of the energetics of the zeolite-SDA systems came later with works such as that by Valyocsik et al. [42] in 1994, and in a more systematic and sophisticated way by Catlow et al. [43].

Following a similar approach we computed in our group the energetics of the system ZSM-18 and the tris-pyrrolidinium cation [44] which is thought to be the only case in which an almost perfect match (free of rotation) between the shape and size of the organic molecule and the zeolite micropore is found, and we found that, apart from the structure directing effect, an additional effect of aluminium preferential location was driven by the organic molecule. The aluminium preferential location was not driven through van der Waals but through electrostatic type of interactions. In fact, most structure directing agents are charged molecules and this fact led us to propose energetic treatments not only based on van der Waals type of interactions, suggesting that other additional energetic terms will come at play in the synthesis of zeolites with SDAs [45,46]. A simple argument helps further to validate our assumption that not only van der Waals interactions contribute significantly to drive the synthesis of zeolites in the presence of SDAs as follows. Zeolites are a large family of porous tectosilicates, which are metastable with respect to quartz with small energetic differences between them, and thus small energetic contributions brought into the system by the introduction of one or other SDA may drive the final energy of the system towards very different zeolitic phases. In the particular case of synthesis in fluoride media, recent computational work helps to rationalise experimental results by taking into account the importance of the electrostatic interactions between charged SDA molecules and fluoride anions, showing that this contribution needs to be taken into account as well as the short range van der Waals interaction between the organic SDA and the zeolite structure [47–49].

#### 5. Epilogue

As has been shown the confinement effect is the most important feature in zeolite science. It could be counter-argued that the above

opinion neglects the chemical composition of the zeolite micropores, without which crucial effects such as active sites would mean to play a secondary role in the chemistry of these materials. But the real fact is that amorphous aluminosilicates (chemically equivalent to zeolites but without microporous environments) are of much less application than zeolites, and this is because the presence of regular (crystalline) micropores in the latter provides a unique feature from which a plethora of possibilities emerge. Having said that, we would like to add that effects of microporous environments were never neglected, not even in the early times where zeolites started to be used on a wide range of applications, but on the other hand, confinement effects were always difficult to systematize. Eric Derouane was one of the first scientists to propose a systematic treatment of the confinement effects of zeolites on the incoming molecules. His treatment was qualitative and quantitative, elegant and fruitful, and the consequences of it were important and cleverly analysed. We believe this represents an indelible contribution whose consequences are still blossoming and fertilising new fields of research in zeolite science.

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