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Self-avoiding walks and connective constants in zeolitic frameworks

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Abstract. The number of self-avoiding walks, u_n , in several zeolitic frameworks has been calculated up to distances n higher than 20 steps. This allows us to estimate the 'connective constant' or effective coordination number of these structures as the limit of the ratio u_n/u_{n-1} for large n . This parameter is correlated with the density of tetrahedra in the zeolite networks, and is shown to be very useful for characterizing the network connectivity, as well as quantifying the influence of the framework topology on the Si, Al atom ordering in these materials.

1. Introduction

Zeolites are aluminosilicates with complex crystal structures, which result from the three-dimensional arrangement of tetrahedral SiO_4 and AlO_4 units sharing corners. These frameworks contain cavities and channels with typical dimensions in the range of 4–12 Å, offering the possibility of trapping atoms and molecules of adequate dimensions in their void space. This property is the origin of a large number of industrial applications of zeolites as catalysts or as molecular sieves [1, 2].

The characterization of zeolitic frameworks by geometrical and topological methods has been a challenge for chemists and materials scientists in the last twenty years. Nowadays, more than eighty zeolite structures are known, and have been well characterized by diffraction and spectroscopic techniques [2, 3]. It is generally accepted that the network connectivity conditions the physical and chemical properties of these materials. In particular, the distribution of tetrahedral atoms (Al and Si) over the framework depends on topological features of the zeolite structures [4–6]. A key point in the framework characterization is thus the search for structural or topological variables quantifying different aspects of these silicate networks and that could be directly related to the physico-chemical properties of the corresponding materials.

Several approaches have been proposed to characterize the topology of zeolite frameworks. Thus, for a particular tetrahedral (T) site in a given zeolite framework, one can define a coordination sequence (CS) as a series of numbers $\{N_k\}$, with $k = 1, 2, \dots$, where N_k is the number of T sites in 'sphere' k which are connected to 'sphere' $k - 1$ [7, 8]. This is a purely topological concept, and the CS for each T atom in a zeolite structure depends only on the topology of the framework, but not on chemical composition, lattice distortions and other structural factors. A concept related to the CS is the so-called coordination degree sequence [9], which gives additional information on the connectivity between successive topological shells. A different approach to studying the topology of zeolites consists in classifying the different materials according to the types of structural subunit (e.g., rings or

polyhedra) contained in their frameworks. An extensive review of this procedure was given by Smith [10].

In this paper, a different way of characterizing the zeolite frameworks is introduced. It consists in calculating the connective constants or effective coordination numbers of these silicate networks, from the long-distance behaviour of the number of self-avoiding walks in the corresponding structures. These concepts are explained in detail in the following paragraphs.

2. Method of calculation

To give a precise definition of random walks in zeolitic frameworks, we will consider a simplified structure obtained by removing oxygen atoms and extraframework cations from a given structure (see figure 1). In this way, we consider T atoms that share a common oxygen atom as being linked to one another in the simplified structure; each T atom is assumed to be linked to four other T atoms, and the resulting structures are fourfold coordinated [11]. A self-avoiding walk (SAW) in a zeolitic framework is then defined as a walk in the simplified structure which can never intersect itself. On a given network, the walk is restricted to moving to a nearest-neighbour site during each step, and the self-avoiding condition constrains the walk to occupy only sites which have not been previously visited in the same walk [12, 13]. To illustrate the application of this definition to zeolitic frameworks, we show in figure 1 (a sketch of the zeolite-A framework) two possible six-step walks, from which only one (indicated by b) is a self-avoiding walk. SAWs have been used for modelling the large-scale properties of long flexible macromolecules in solution [12, 14], as well as for the study of polymers trapped in porous media, gel electrophoresis, and size exclusion chromatography, which deal with the transport of polymers through membranes with very small pores [15]. They have been also employed in the analysis of critical phenomena in lattice models [13, 16]. Universal constants for self-avoiding walks have been discussed in a review by Privman *et al* [17].

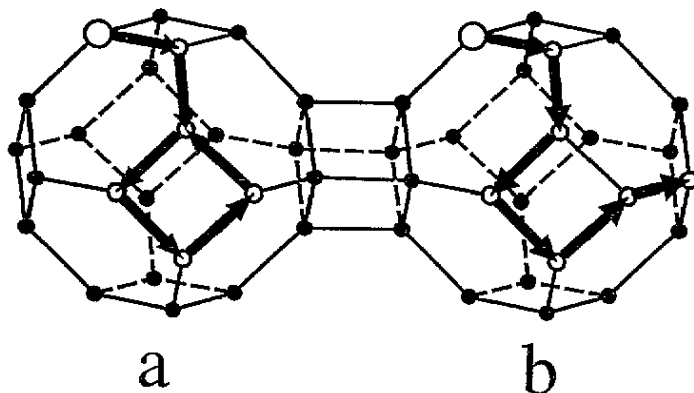


Figure 1. A sketch of the zeolite-A framework (structure of Linde-A type) showing two possible six-step walks starting from the sites indicated by large open circles. The sites visited are indicated by small open circles. The walk on the right (b) is a self-avoiding walk, but that on the left is *not* (a). Only T sites of the framework are shown. O atoms, located approximately half-way between tetrahedral atoms are omitted for simplicity.

The formulas governing the asymptotic behaviour of SAWs are significantly different from those of free walks. If we use the term u_n for the number of different SAWs starting

from a given lattice site, its asymptotic behaviour for large n is given by [17, 18, 19]

$$u_n \sim n^{\gamma-1} \mu^n. \quad (1)$$

γ is a critical exponent with values $\sim 7/6$ for three-dimensional structures, and μ is the so-called 'connective constant' or effective coordination number of the corresponding structure [12, 18, 19]. This (non-universal) parameter μ can be obtained from equation (1) by taking the limit

$$\mu = \lim_{n \rightarrow \infty} \frac{u_n}{u_{n-1}}. \quad (2)$$

The connective constant depends upon the particular topology of each structure, and has been determined very accurately for standard 3D lattices. In particular, for the diamond structure (with the same coordination as our simplified silicate frameworks, $z = 4$), one has $\mu = 2.8792$ [18]. In general, for a structure with coordination number z , one has $\mu \leq z - 1$ [12].

3. Results and discussion

We have calculated the numbers u_n of SAWs for eight zeolitic frameworks by counting the possible walks up to $n = 21$ in large supercells including about 15 000 T sites. The u_n so obtained are presented in table 1 for several values of n . In connection with this, we note that for the so-called Bethe lattice (or Cayley tree) [11, 20], which does not contain any loop, the number of SAWs is given exactly by $u_n^{BL} = z(z-1)^{n-1}$. This means that for $z = 4$ one has $u_5^{BL} = 324$, and the lower values of u_n for the zeolite frameworks are due to the presence of structural rings with five or fewer T sites. Since the frameworks considered in this work include only rings with even numbers of T sites, u_5 depends only on the number of four-membered rings in each structure. In fact, this is the result shown in table 1, as for increasing number of tetramer rings per T site, the number u_5 decreases consequently. For longer SAWs (larger n), loops with higher numbers of sites contribute to reducing the number u_n with respect to that of the Bethe lattice. Values of the connective constants μ obtained by using equation (2) are also given in table 1. We estimate for the μ -values presented here an error bar of ± 0.002 , due basically to the extrapolation $n \rightarrow \infty$. For the Bethe lattice with $z = 4$, one has $\mu = 3$.

Table 1. The number u_n of SAWs of different lengths n for several zeolitic frameworks, along with the corresponding connective constants μ . For offretite and phillipsite, which contain topologically non-equivalent tetrahedral sites, average numbers are given. Values for the diamond structure are also shown for comparison.

Zeolite	$n = 5$	$n = 10$	$n = 15$	$n = 20$	μ
Faujasite	294	52 100	8 840 176	1 462 364 178	2.749
Linde A	294	51 004	8 655 262	1 440 218 448	2.759
Offretite	297	54 811	9 669 160	1 673 878 658	2.779
Chabazite	294	52 956	9 269 214	1 593 555 470	2.780
Phillipsite	294	54 350	9 772 744	1 723 800 790	2.789
Cancrinite	304	59 194	11 096 960	2 042 690 698	2.815
Sodalite	304	60 720	11 703 776	2 213 358 896	2.829
Analcime	304	61 728	12 071 624	2 317 661 564	2.839
Diamond	324	70 188	14 774 652	3 051 900 516	2.879

A parameter of zeolite structures interesting for comparison with the topological variables is the framework density (FD), defined as the number of tetrahedral atoms per unit volume (nm^{-3}). This structural parameter has been used by several authors in different studies of tectosilicates, and zeolites in particular [3, 11, 21]. However, the FD for compounds with the same network but differing chemical composition can change appreciably [11]. Thus, to assign more precisely a FD for each tectosilicate structure it is convenient to define a normalized framework density (FD^*), which reduces the effect of lattice dilation or contraction due to chemical composition. With this purpose, Stixrude and Bukowinski [11] defined FD^* as the framework density scaled to a standard T-T distance, which they chose to be $L_S = 3.1 \text{ \AA}$. For a given tectosilicate structure one has

$$\text{FD}^* = \text{FD} (L/L_S)^3 \quad (3)$$

where L is the average T-T distance of the material under consideration. In figure 2 we present the parameter μ of the zeolite frameworks studied here versus the normalized framework density. It is clear that there exists a correlation between the two quantities (correlation coefficient, $\rho = 0.975$), reflecting the natural fact that the connective constant goes up as the density of tetrahedral sites increases.

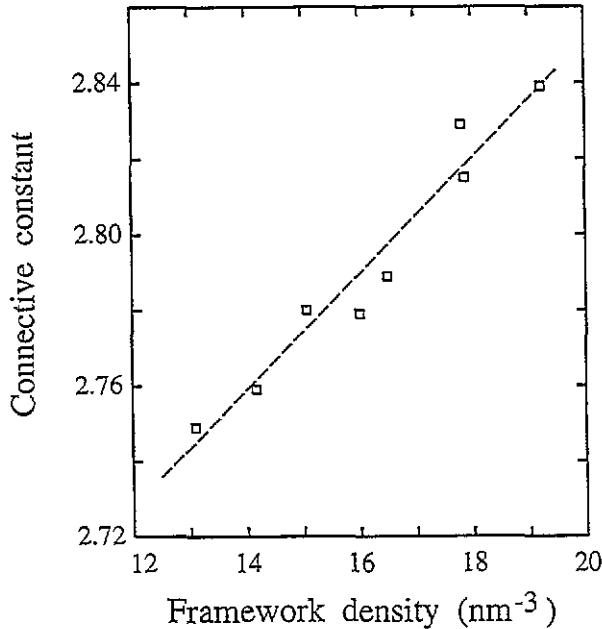


Figure 2. The connective constant (μ) versus the normalized framework density (FD^*) for several zeolite frameworks. The dashed line is a least-squares fit to guide the eye.

Connective constants are especially suitable for quantifying the influence of the framework topology on the tetrahedral atom ordering in aluminosilicate materials. As an example, we have studied the correlation between the parameter μ and the transition temperature for a lattice-gas model in the zeolite networks [5, 22]. In this simple model, we associate with each site i the variable σ_i , which equals 1 or 0 according to whether the site is occupied by an Al or a Si atom, and the energy of an atom configuration is given by

$$U = \epsilon \sum_{i,j} \sigma_i \sigma_j \quad (4)$$

where the sum is extended to nearest T neighbours, and ϵ represents an effective repulsive interaction between aluminium atoms in nearest T sites ($\epsilon > 0$). This model is based on the experimental evidence for the avoidance of Al atoms in adjacent tetrahedra (Loewenstein's rule) [23, 24]. The Si, Al atom distribution has been simulated with this model by a Monte Carlo procedure for the eight zeolite structures considered here. The atomic fractions of Al and Si were taken to be equal ($x_{Si}/x_{Al} = 1$). More detailed descriptions of this kind of Monte Carlo simulation can be found elsewhere [5, 12] and will not be repeated here. It is well known that such a lattice-gas model presents a temperature-driven second-order phase transition from a low-temperature long-range-order pattern (Al and Si atoms alternate in the framework) to a high-temperature atom distribution with only short-range order [20, 22]. Moreover, it has been previously shown that the calculated critical temperature for this transition in aluminosilicates depends on the network topology, and in particular on the number N_2 of next-nearest tetrahedra in the framework [5].

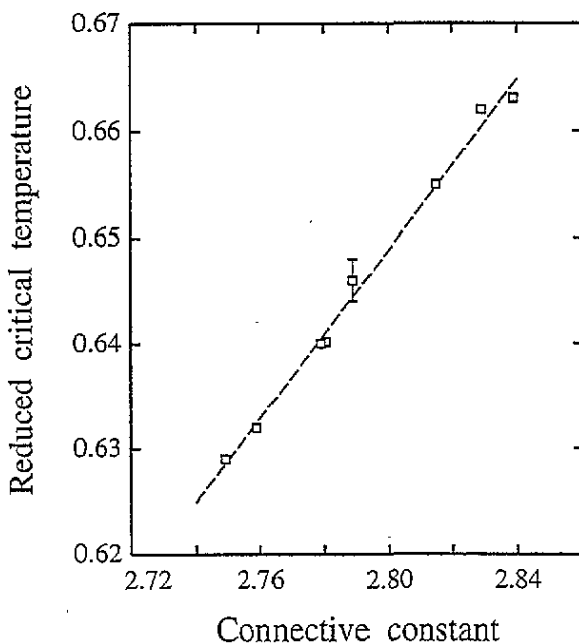


Figure 3. The dependence of the critical temperature for a lattice-gas model upon the connective constant of the framework. The reduced temperature τ is defined as $\tau = k_B T / \epsilon$ (k_B : the Boltzmann constant). The dashed line is given by $\tau = a\mu + b$, with $a = 0.399$ and $b = -0.469$. The estimated error in the reduced critical temperatures is ± 0.002 .

The dependence of the critical temperature (T_c) on the connective constant μ of the zeolite networks is shown in figure 3. We find a linear dependence for the eight tectosilicate structures considered here ($\rho = 0.996$). For increasing connective constant, the critical temperature goes up, indicating that higher μ favours the long-range order in the atom distribution. This is consistent with the intuitive fact that increasing the effective coordination number favours the propagation of atom ordering through the network. As one could expect, the correlation between T_c and μ shown in figure 3 is much better than that found between T_c and N_2 [5], since μ takes into account the whole topology of the framework and not only the local connectivity up to next-nearest tetrahedra. The correlation between T_c and other framework-dependent parameters described in the literature is also

poorer than that obtained for μ . Thus, for the framework density FD^* we find $\rho = 0.968$, and for the so-called topological density [3, 21], $\rho = 0.913$.

Similar correlations are expected to be found between the connective constant and other framework properties, such as the site percolation threshold, a parameter related to the maximum concentration of substitutional species that can be present in these tetrahedral networks [4, 25]. The calculation of the number of self-avoiding walks and connective constants presented here for zeolites can be directly generalized to other tectosilicates with non-zeolitic frameworks. Also, the actual values of the parameters found for the line $\tau_c = a\mu + b$ presented in figure 3 ($a = 0.399$, $b = -0.469$) require further investigation. Another interesting point to be investigated in the near future is the dependence of the so-called radius of gyration of the walks [17] on the aluminosilicate framework, as well as the calculation of universal quantities related to it.

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