Application of Boltzmann's Integration Method under non-ideal Conditions

Lars Heinke

Fakultät für Physik und Geowissenschaften, Abteilung Grenzflächenphysik, Linnéstr. 5,

04103 Leipzig, Germany

E-Mail: Heinke@physik.uni-leipzig.de

Abstract

Boltzmann's integration method may prove to be a very powerful tool to study the transport diffusion of guest molecules in nanoporous host systems. In many cases, however, the prerequisites for applying this method are not completely fulfilled. In the following, the consequences of these deviations on the accuracy of the obtained results are discussed. It is found that the results of Boltzmann's integration method can be corrected by different considerations. The discussion is focussed on the concentration profiles observed during the adsorption and desorption of methanol in ferrierite-type crystals as observable by interference microscopy.

Keywords: Boltzmann's integration method, diffusion, nanoporous materials

Introduction

Mass transport of guest molecules in nanoporous host materials is an important field of science with application in basic research as well as in the chemical industry. In a number of scientific works the intracrystalline diffusion is studied by analysing the integral uptake averaged over the whole sample [1-4]. The recently developed interference microscopy method [5] is able to monitor the intracrystalline concentration profiles of one single crystal with a sufficient spatial and temporal resolution. The received data provide a lot of information which can not be received by integral techniques.

To determine the relevant transport parameters, namely the diffusivity and the surface permeabilities, new methods in analysing these profiles have been introduced. The surface permeability can be calculated by relating the flux through the surface to the actual surface concentration. For determining the transport diffusivity there exists the direct way of applying Fick's 2nd law. Though this most direct access has been successfully applied in

several cases [6-8], its efficiency is limited by a couple of disadvantages. (i) Direct application of Fick's 2nd law is only possible in the central part of the profiles where the first spatial derivative of the concentration becomes zero. (ii) The accuracy of the resulting diffusivities is notably impaired by the noise of the data points. (iii) Each value in the concentration dependence of the diffusivity needs a separate calculation.

An indirect way to obtain transport diffusivities is provided by the Boltzmann transformation leading to Boltzmann's integration method [9]. This approach, however, is restricted to some restraints, viz. the diffusion has to be one-dimensional and the external surface must not exhibit any resistance to mass transfer. These restrictions are hardly strictly fulfilled. In the following, we are going to discuss the effects which small deviations from the prerequisites might have on the final results.

In particular we are going to discuss the application of Boltzmann's integration method to analyse the evolution of the concentration profiles during the uptake of methanol by ferrierite. Though this system exhibits favourable conditions for the application of this method, we shall see that the prerequisites are not completely fulfilled.
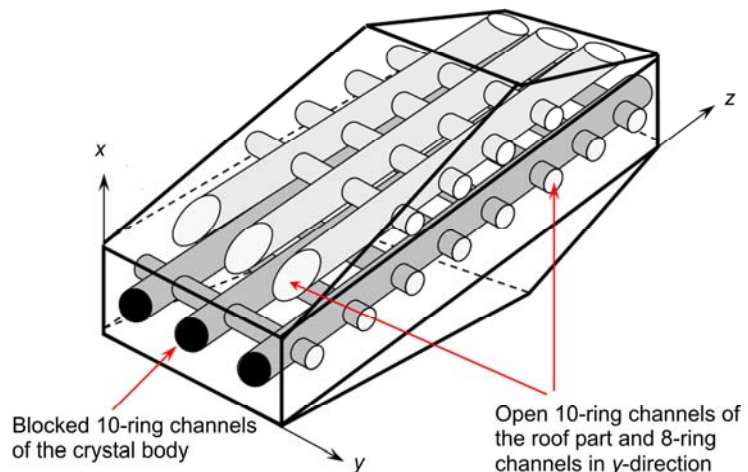

Experimental results

The ferrierite zeolite is a cation-free zeolite with two perpendicular channel systems which intersect each other [10]. One system of channels is adjusted along y-direction and is framed by eight-membered rings, this means they are formed by eight oxygen and eight silicon atoms [7]. The other channel system is along z-direction and is formed by ten-membered ring channels. Due to the larger diameter of the channels along z, a higher diffusivity can be assumed there.

The outer geometry is like a cuboid with a short side length in x-direction ($l_x = 10$ μm), and two long side lengths in y and z ($l_y = 50$ μm, $l_z = 220$ μm). On each of the two big side faces of the crystal there are small roof-like parts (fig. 1).

The entity of concentration profiles recorded during the uptake and release of methanol on such crystals by means of interference microscopy (IFM) is presented in [7]. These profiles have a spatial resolution of 0.5 μm and a temporal resolution of up to 10 s. The direction of monitoring the concentration profiles is along x. There are no channels in this direction, so that mass transport is excluded and concentration in the cuboid-like central part is constant in x-direction.

Figure 1: Ferrierite crystal with a two-dimensional pore structure. The figure shows partially blocked channels in *z*-direction in the main body of the crystal, open channels in *z*-direction in the roof section and open channels in *y*-direction [7].

Blocked 10-ring channels of the crystal body

Open 10-ring channels of the roof part and 8-ring channels in *y*-direction

In the observed concentration profiles (fig. 2) it is visible that the concentration in the roof-like part of the crystal is built up instantaneously. Hence, this part of the concentration can easily be subtracted to yield the concentration in the central part of the crystal (fig. 3). In this cuboid-like part there exists no concentration gradient along *z*-direction and the concentration has not reached the equilibrium value. Consequently, the surface permeability into these big ten-membered ring channels is very low or zero. Furthermore, the concentration profiles along *y*-direction are curved (see fig. 3), so that the main part of the mass transport is along these channels. The concentration close to the crystal surface in *y*-direction is smaller than the equilibrium value. Therefore, this surface is also a resistance to the mass transport. This means the surface permeability is not infinitely large.

Figure 2: Concentration profiles measured during adsorption for the pressure step of 0 to 80 mbar. The concentration is normalized with respect to the maximum value in the roof [7].
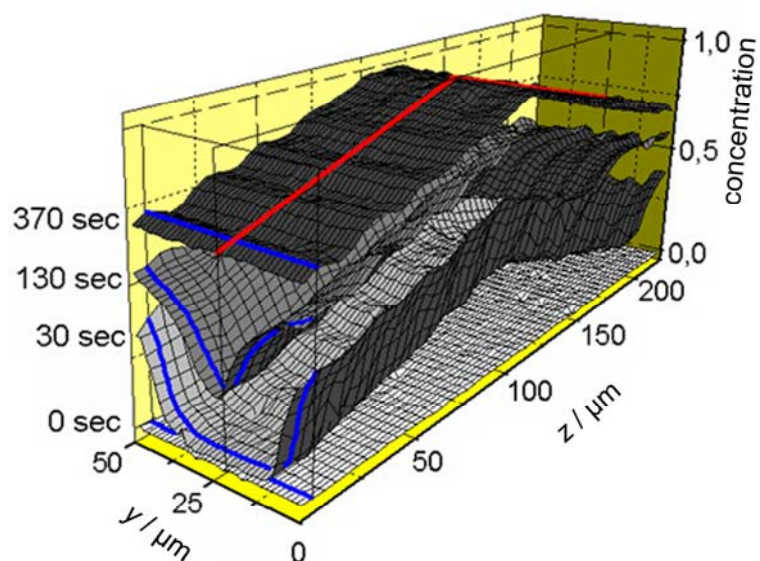
From the slowly increasing concentration in the centre of the profiles in *y*-direction at small times (t = 30 s ... 90 s in fig. 3), without any concentration gradient along *y*, one has to conclude that mass transport is not completely restricted to this direction. So, taking the topology of the ferrierite into account, one may conclude that some mass transport has to proceed also along *z*-direction.

Figure 3: Concentration profiles in *y*-direction measured during adsorption for the pressure step of 0 to 80 mbar [7].
Up to 110 s after onset of adsorption the fronts of molecular concentration that have penetrated through the two apposed crystal faces in *y*-direction do not overlap.
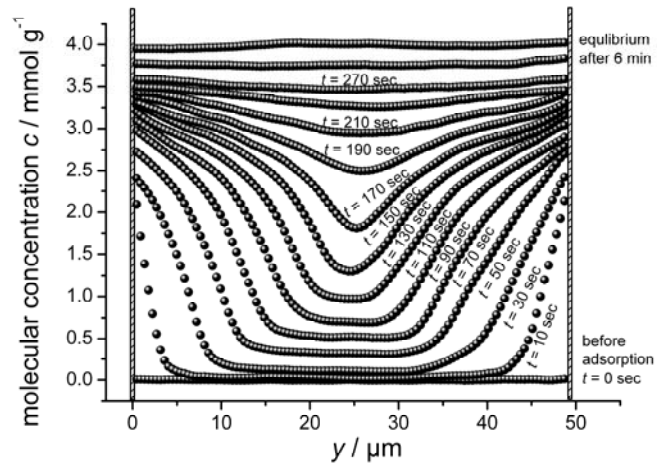
To sum up, mass transport in these crystals is dominated by diffusion in *y*-direction, where uptake is affected both by diffusion in the channels and by a reduced surface permeability. The rate of uptake in *z*-direction is much smaller. It is controlled by the small surface permeability, since the diffusivity along *z* is very large because of the bigger channel diameter. Therefore, there exist no measurable concentration gradients in the cuboid central part, this means $c(y,z) = c(y)$.

Boltzmann's integration method

The concentration profiles measured by IFM have a sufficient spatial and temporal resolution which allows their thorough analysis. In [7], analysis of these profiles by a differential application of Fick's 2nd law has been shown to yield transport diffusivities ranging over close to two orders of magnitude. This type of analysis, however, is impaired by the significant statistical noise of the individual data points and the small number of data points used to determine the diffusivities for each particular concentration.

Another, integral approach to determine diffusivities from the concentration profiles is based on the Boltzmann-transformation [11, 12]

$$\eta = \frac{y}{\sqrt{t}}. \tag{1}$$

By using this substitution, for uptake by a semi-infinite medium without surface barrier (i.e. with infinite surface permeability) Fick's 2nd law for one-dimension

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y}\left(D \frac{\partial c}{\partial y} \right) = D \frac{\partial^2 c}{\partial y^2} + \frac{\partial D}{\partial c}\left(\frac{\partial c}{\partial y} \right)^2 \tag{2}$$

may be written as

$$-\eta \frac{dc}{d\eta} = 2\frac{d}{d\eta}\left(D \frac{dc}{d\eta} \right). \tag{3}$$

The relevant boundary and initial conditions for this transformation from y to η are $c(y=0, t) = c_{eq}$ at the crystal surface and $c(y\rightarrow\infty, t) = c(y, t=0)$.

   Substitution by eq.(1) is thus found to transform the partial differential equation (2) with concentration c depending on time t and space y into an ordinary differential equation (3) where c now depends on only one variable η. The big benefit of this procedure becomes obvious after integrating eq.(3) over this new variable from $\eta = \infty$ to $\eta\,(c)$ and transposing to D:

$$D\big(\eta(c)\big) = -\frac{d\eta}{dc}\cdot\int_0^c \eta dc'. \tag{4}$$

   This relation, after resubstitution of η, provides an equation which allows a direct calculation of the transport diffusivity D in dependence on concentration c for one concentration profile $c(y)$ measured at one sole point in time t (fig. 4):

Figure 4: Application of Boltzmann's integration method to a concentration profile ($D = \exp(5{\cdot}c)\,10^{-13}\ \mathrm{m^2 s^{-1}}$ and $t = 30$ s).
The integral (yellow area) and the derivative (red arrow) of eq. (5) are indicated for a relative concentration of 0.6.
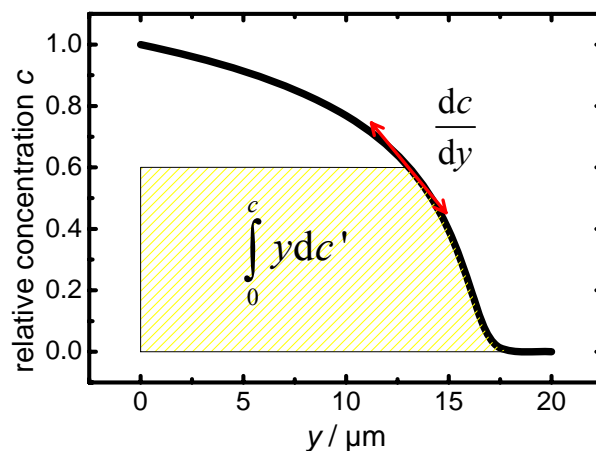
$$D\big(c(x,t)\big) = -\frac{1}{2t}\left(\frac{dc(y)}{dy}\right)^{-1} \cdot \int_0^c y(c')dc' \qquad (5)$$

This method can also be used for analysing the initial period of molecular uptake by finite, one-dimensional systems, namely, if the time considered is small enough so that the concentration profiles of the molecules which penetrate through the two apposed crystal faces into the channel system do not yet overlap. In such cases, each branch of the concentration profiles can be considered as semi-infinite.

If these prerequisites are fulfilled Boltzmann's integration method yields very precise results with very low statistical noise and a large amount of data points (fig. 5). In view of the great potentials of the Boltzmann's integration method it is worthwhile to analyse in more detail the consequences of possible deviations from the required prerequisites on the final results.

Figure 5: Diffusivity from concentration profile in fig. 4 calculated with Boltzmann's integration method. This result corresponds with the original diffusivity.
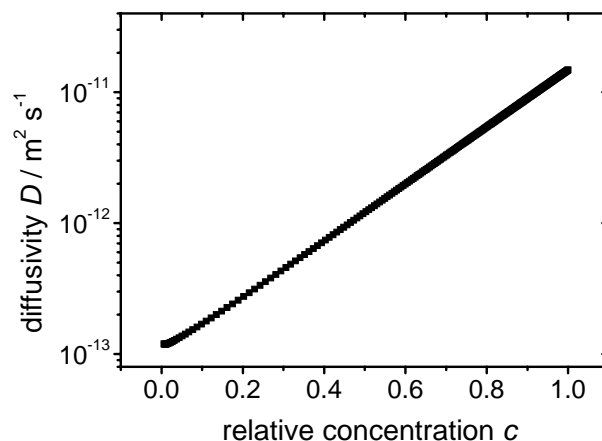
Application of Boltzmann's integration method to methanol in ferrierite

The considerations of methanol transport in ferrierite have led us to fig. 6, in which only those molecules are recorded which have entered the ferrierite crystals along the channels in y-direction. Moreover, it turns out that, till about 90 seconds after the onset of the adsorption process, the thus determined normalized concentration profiles are in reasonable accordance with the initial and boundary conditions required to the application of Boltzmann's integration method (with the initial loading $c(y,t{=}0) = c_0$ being equal to zero). The mutual encounter of the diffusion fronts in the crystal centre after about 100 s terminates the time range of its application.

Figure 6: Normalized concentration profiles, resulting after subtraction of molecular uptake through the 10-membered ring channels in *z*-direction
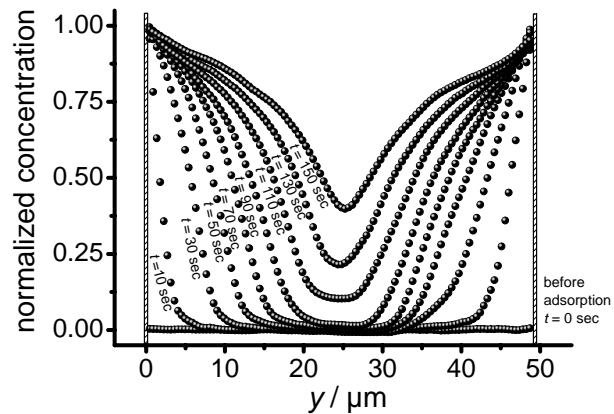
The plots of these concentration profiles as a function of the unifying variable $\eta = y/\sqrt{t}$ are displayed in fig. 7. Obviously, in contrast to the behaviour expected on the basis of eq. (3), there is no complete coincidence between the different plots of the diffusion fronts entering in $\pm$ *y*-direction on either face of the crystal. We have to accept these differences as an indication that the prerequisites of Boltzmann's integration method are not ideally fulfilled. It shall be the task of the next section to identify the origin of these shortcomings and to estimate their influence on the obtained data.
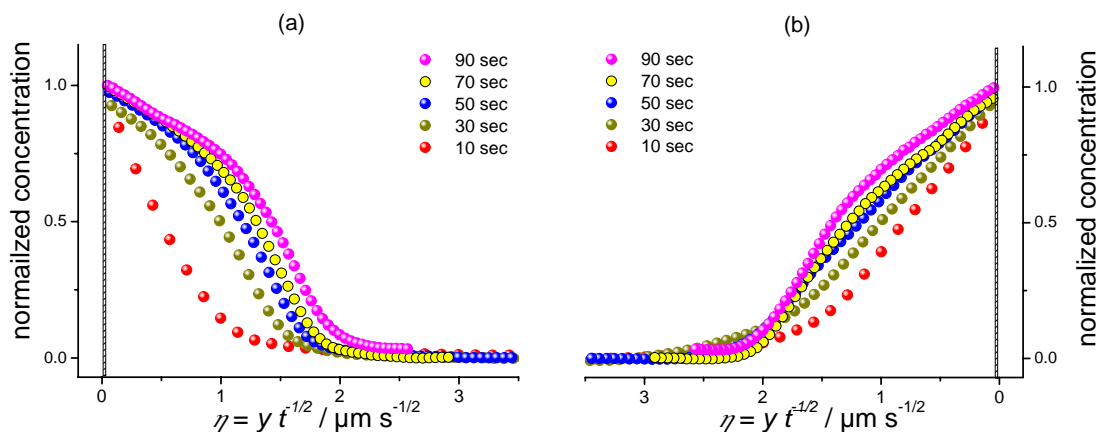

Figure 7: Evolution of the methanol concentration profiles in *y*-direction in the left (a) and right (b) side of the ferrierite crystal as a function of the parameter $\eta = y/\sqrt{t}$.

Fig. 8 provides an overview of the diffusivities determined from the uptake profiles after 70 and 90 seconds on both sides of the crystal. For comparison, we have also indicated the data points which have been determined previously, by conventional data analysis on the basis of the differential (microscopic) use of Fick's 2nd law [7]. These data represent the

extract of several adsorption - desorption cycles with varying initial and final pressures. Though the agreement between the results of different runs confirms the reliability, the procedure proves to be rather time consuming. By contrast, the primary data used for the application of Boltzmann's integration have been determined during a single run within not more than 100 s!
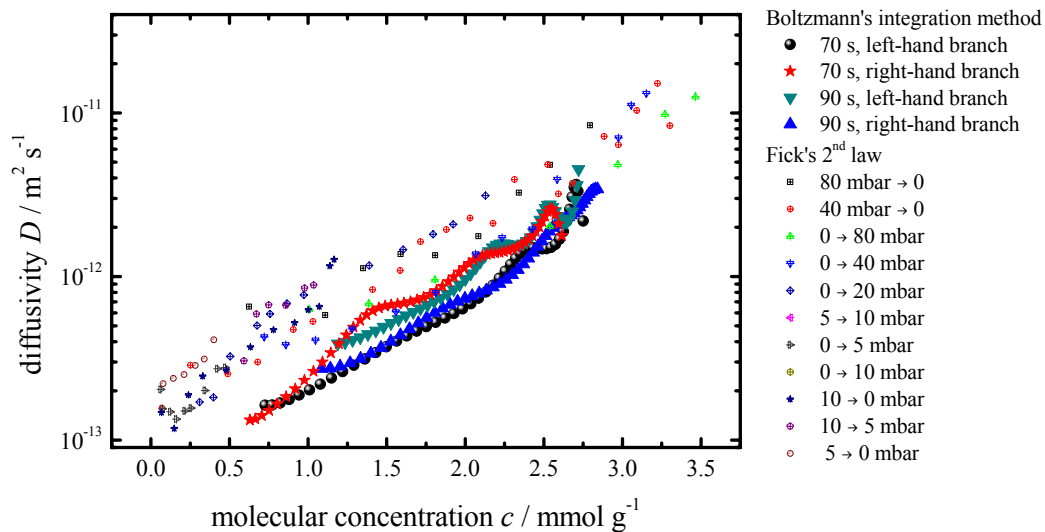

Figure 8: Diffusivity of methanol in ferrierite calculated by Boltzmann's integration method for a pressure step of 0 to 80 mbar at $t = 70$s and $t = 90$s [12]. The violation of the prerequisites for this method is expected to lead to deviations from the correct data. The diffusivity calculated by Fick's 2nd law for several pressure steps is also shown.

Most remarkably, both data sets indicate a dramatic concentration dependence of the diffusivities which increase by close to two orders of magnitude with increasing concentration. By contrast, the difference in the absolute values of the diffusivities determined either differentially from Fick's 2nd law or by Boltzmann's integration method amounts to not more than a factor of 2. In the literature [13-15] differences over several orders of magnitude are not unusual for intracrystalline diffusivities measured by different techniques. The origin of these differences is generally referred to the different space scales over which the diffusion phenomena are recorded by these different techniques. Interference microscopy is the first technique to yield space-resolved intracrystalline transport diffusivities. Boltzmann's integration method represents a valuable test to check whether the behaviour of the total concentration front on passing the crystal turns out to be compatible with the microscopic predictions on the basis of a local application of Fick's 2nd law. The

coinciding trends of the representations of fig. 8 indicate that, over the total range of guest concentrations, the transport properties of the nanoporous crystal under study adequately reveal its microscopic behaviour, i.e. any notable influence of additional transport resistances (like internal barriers as observed, e.g., in [16-19]) may be excluded. By discussing and evaluating the limitations of the application of Boltzmann's integration method to the present system in the following, we shall illustrate, that the differences in the two sets of data evaluation may be attributed to these limitations.

Shortcomings in the prerequisites of Boltzmann's integration method and options of compensation

As already shown, the prerequisites for this technique are not completely fulfilled, so it is important to discuss the influence of these two deviations, namely the influence of a (small) surface resistance and a (small) contribution to the molecular uptake by the channel system perpendicular to the considered one in y-direction.

First, we are going to discuss the influence of the reduced surface permeability in y-direction. As a first approximation for including the influence of the surface resistance in an estimate of the diffusivity by Boltzmann's integration method, we replace the effect of the surface resistance by a virtual enlargement of the crystal over a certain distance l^* (fig. 9), so that an extrapolation of the concentration profiles from the crystal investigated into a virtually enlarged range leads to the equilibrium boundary conditions.

This enlarged concentration profile has the shape of a completely diffusion-controlled profile. Hence, by adapting Boltzmann's integration method to this virtually enlarged profile, the diffusivity may be correctly calculated using the relation

$$D\big(c(y,t)\big) = -\frac{1}{2t}\left(\frac{dc(y)}{dy}\right)^{-1} \cdot \int_0^c \big(y(c')+l^*\big)dc'. \tag{6}$$

Therefore, in systems where a surface barrier reduces the surface concentration, the correct values of the transport diffusivity can be calculated by elongating the concentration profiles by a suitably chosen length l^* so that the extended profile seems completely diffusion-controlled. l^* can be estimated very well by elongating the profiles with the slope at the profiles edge. Finally, the thus calculated diffusivities can be used to simulate the concentration profiles and to check the accuracy of the estimated length l^*.

Figure 9: Concentration profile where mass transport is controlled by diffusion and surface resistance (thick black line). The thin red line visualises the virtual enlargement of the concentration profile by a certain length l^*. (Parameters used for this example: $D = 10^{-13}$ m^2 s^{-1}, $\alpha = 2 \cdot 10^{-8}$ m s^{-1}, $t = 300$ s, $l = 20$ µm and $l^* = 4.4$ µm)
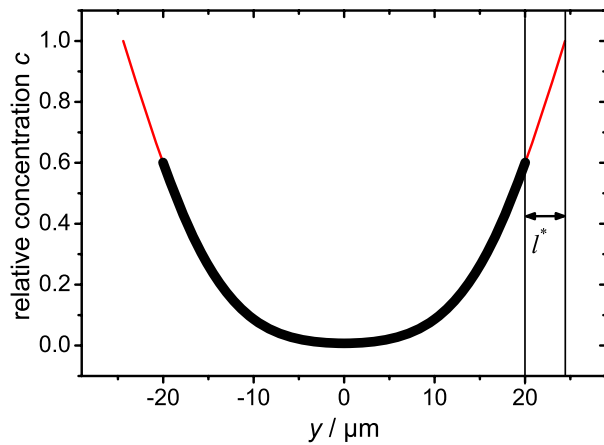
In the given methanol concentration profiles in ferrierite for a time of 70 s and 90 s after onset of adsorption the extension length l^* results to be about 12 µm (fig. 10). By comparing the results obtained by the application of eqs. (5) and (6), respectively, the application of Boltzmann's integration method without consideration of surface resistance is found to yield diffusivities which are by about 35 % smaller than the correct values.

Figure 10: Concentration profiles of methanol in ferrierite as observed by interference microscopy for a gas pressure step from 0 to 80 mbar, $t = 70$ s and $t = 90$ s [7].
Profile extension length l^* to correct for the influence of surface barriers and concentration enhancement c_0 in the profile centres which is brought about by diffusion in z-(rather than in y-) direction are also indicated.
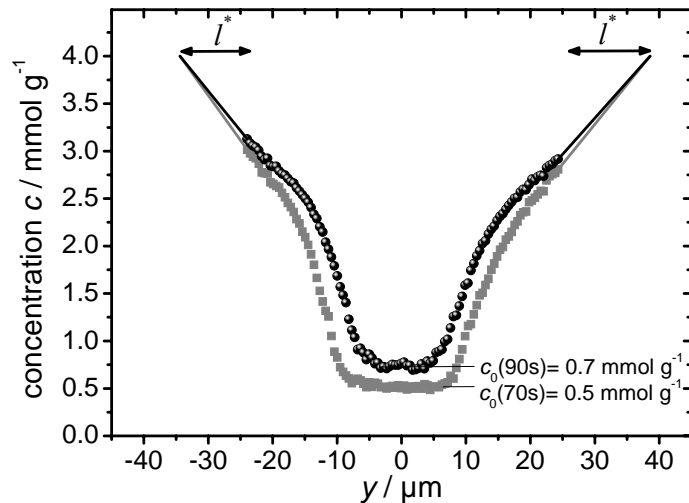
Deviations from strictly one-dimensional diffusion are more difficult to handle with Boltzmann's integration method. Since molecular concentrations in the centre (i.e. flat) parts of the profiles are found to increase (which for strictly one-dimensional diffusion would be forbidden by Fick's 2nd law), we have to imply that there is as well a small contribution to

overall mass transfer by diffusion in z-direction. This means, that there is some finite permeability through the obstructed ends of the channels in z-direction. Owing to the large diameter of these channels (and the finding that the roof-like parts, with open apertures, are essentially instantaneously filled) one may assume that the concentration of these molecules is constant all over the crystal. To estimate the influence of this mass transfer in z-direction, it is reasonable to distinguish molecular concentrations according to the direction in which the respective molecules entered the crystal. We simplify our further discussion by assessing that at any time the concentration c_z of these molecules which have entered along z-channels is uniform over the crystal, i.e. $c_z(y,z)=c_z$. For small times, when the concentration fronts have not yet met, c_z may directly be taken from the concentration in the centre of the profiles (c_0 in fig. 10). Adapting Boltzmann's integration method to this situation leads to

$$D(c) = -\frac{1}{2t}\left(\frac{dc}{dy}\right)^{-1} \cdot \int_{c_0}^{c} y(c')dc' .$$
(7)

Since, by doing so, we have neglected all molecules which have entered the crystal along the second direction, we expect that the results of eq.(7) deviates from the actual diffusivities.

Figure 11: Concentration profiles for one- and two-dimensional mass transport. The derivative and integral are depicted in blue for the two-dimensional case (eq.(7)) and in green for the one-dimensional case (eq.(5)). The inverse derivative $(dc_{2d}/dy)^{-1}$ is generally larger than $(dc_{1d}/dy)^{-1}$, whereas $\int_{c_0}^{c} y(c_{2d}')dc'$ is commonly smaller than $\int_{0}^{c} y(c_{1d}')dc'$.
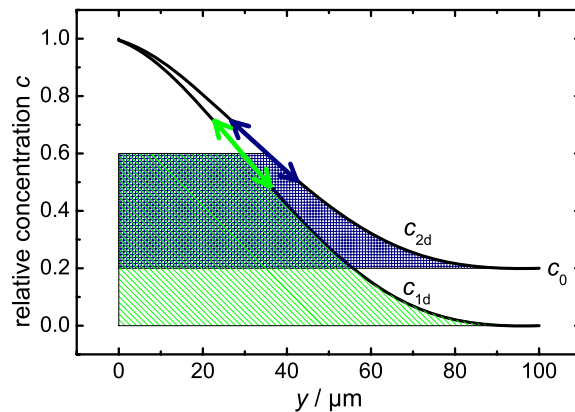
To estimate the influence of the concentration c_0, we assume that c_0 is small and that the contribution by the molecules entering from z-direction does not change the shape of the concentration profiles in y-direction. This means that the finite value of c_0 does only lead to a compression of the concentration profiles following the relation

$$c_{2d}(y,c_0) = \left(1-\frac{c_0}{c_{eq}}\right)c_{1d}(y)+c_0 .$$
(8)

Here, c_{2d} denotes the concentration profiles observed by IFM in which mass transport appears to be two-dimensional. c_{1d} denotes the concentration profiles one would observe for completely one-dimensional mass transport. Figure 11 illustrates the consequences one has to expect by neglecting the concentration of those molecules which entered along z-direction in comparison with the original procedure.

On applying Boltzmann's integration method on both c_{1d} and c_{2d} one finds that the diffusivity for the two-dimensional case (c_{2d} in eq.(7)) is about 20 % smaller than for the one-dimensional case (c_{1d} in eq.(5); c_0/c_{eq} is about 0.15).

Discussion of the correction procedure

We are now going to consider up to which extent the shortcomings in the prerequisites of Boltzmann's integration method may be remedied by the suggested correction method. We shall base our discussion on transient concentration profiles which have been generated with the intracrystalline diffusivities and surface resistances derived from the actual profiles of transient methanol sorption in zeolite ferrierite by microscopic application of Fick's 1st and 2nd laws. In [6, 7], the following concentration dependencies were found to yield satisfactory agreement with the experimental data: the diffusivities are $D_y = \exp(1.7\,c^{0.75})\ 10^{-13}\ m^2\ s^{-1}$ and $D_z = 10^{-7}\ m^2\ s^{-1}$ (which is big enough so that there is (almost) no concentration gradient along z) and the surface permeabilities are $\alpha_y = (2.4 + 0.11\exp(0.75\,c))\ 10^{-7}\ m\ s^{-1}$ and $\alpha_z = 2.6\ 10^{-7}\ m\ s^{-1}$ (c in mmol g^{-1}). The intracrystalline concentration at the beginning is 0, the finally attained equilibrium value c_{eq} is 4 mmol g^{-1}. On the basis of such given dependencies, the corresponding profiles may be simulated by a *Finite Difference Solution* algorithm [9, 20]. The simulation procedure may in particular be applied to such cases, in which only one of the two deviations from the correct prerequisites is abandoned, i.e. one may consider the deviation for ideal one-dimensional diffusion (but with surface resistances) or for two-dimensional diffusion, without additional surface resistance in y-direction.

Application of eq.(7) to the concentration profiles resulting from the complete set of transport parameter, i.e. adapting to the disturbing influence of diffusion in z-direction but leaving the influence of surface barriers uncorrected, leads to values of D_y which are by about 40 % smaller than the D_y value used in the simulations. If diffusion in z-direction is totally excluded in our simulated profiles (and if, consequently, there is no need for this correction anymore) application of the (unmodified) starting eq. (5) yields diffusivities which are about 35 % below the "correct" data. Using the compensation procedure, in the previous section

neglecting the influence of surface barriers was found to lead to diffusivities of about 35 % below the correct values. This estimate is nicely confirmed by the present considerations.

Let us now consider exclusively the disturbing influence of diffusion in z-direction. For this purpose, we have to set α_y equal to infinity (corresponding to negligibly small surface barriers) and to leave all other parameters unchanged. In this case, the diffusivity D_y resulting from the application of Boltzmann's integration method is by about 10% too small. This result deviates from the estimate at the end of the previous section (based on eq. (8)), where the diffusivity following by the application of Boltzmann's integration method (eq.(7)) is reckoned to be by about 20 % too small. Again, however, it is confirmed that, for the system under discussion, the main source of divergence between the correct results and the application of Boltzmann's integration method is due to the external surface barriers.

Unanimously, as an effect of these resistances, application of Boltzmann's integration method (with adaption to only mass transfer in z-direction) has been found to yield values which represent about 60% of the correct ones. Fig. 12 compares the results of Boltzmann's integration method, multiplied with the thus estimated factor of 1/0.6, with the microscopically determined diffusivities.
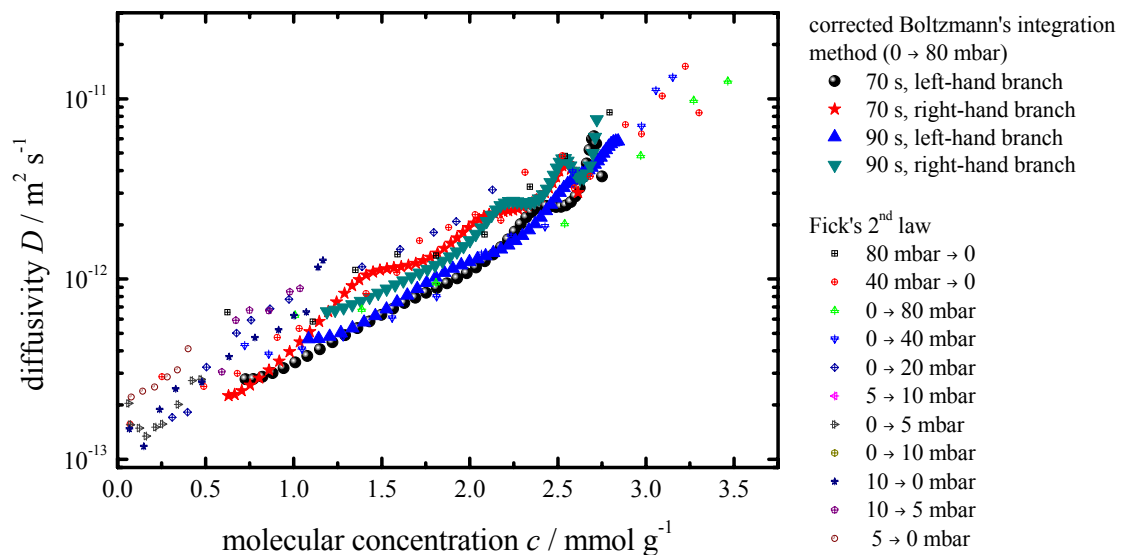

Figure 12: Diffusivity of methanol in ferrierite calculated by Boltzmann's integration method. The results are corrected by a factor of 0.6^{-1}. The diffusivities calculated by Fick's 2nd law for several pressure steps are also shown.

The corrected results of Boltzmann's integration method are found to be in very good agreement with the results of the microscopic (differential) application of Fick's 2nd law (fig. 12). In comparison with the latter technique, Boltzmann's integration method offers the advantage of a greater statistical wealth and the possibility to determine the diffusivities over the entire concentration range out of one concentration profile observed at one sole point in time. Furthermore, by analysing the concentration data with Boltzmann's integration method one adsorption experiment with a big pressure step yields the diffusivity over just this large concentration range covered by the step, whereas for the differential analysis by Fick's 2nd law many sorption experiments are necessary to cover the same concentration range.

Conclusions

The transport properties of guest molecules are crucial features of nanoporous host materials. Therefore, the diffusivity is among the key quantities for their practical performance. Recently, the transport diffusivity of guest molecules in nanoporous host materials has for the first time been calculated in a direct way by a microscopic application of Fick's 2nd law to the intracrystalline concentration profiles as accessible by interference microscopy. This analysis may be dramatically facilitated by means of Boltzmann's integration method which provides a straightforward means to correlate the concentration dependence of the diffusivity with the transient concentration profiles evolving during molecular uptake or release [12]. However, the prerequisites for applying this method may be violated, e. g., by the fact that mass transport is not restricted to one dimension and that the crystal surface as well represents a resistance to the mass transport. Considering the adsorption/desorption behaviour of methanol on ferrierite, it is shown in the present paper that the errors occurring due to the violation of these restraints can be estimated and corrected by detailed analysis. Furthermore, it follows that the surface barrier causes the main part of the error. This influence can be determined very well by a virtual enlargement of the concentration profiles. The estimated deviations of the results of Boltzmann's integration method from the correct values are verified by applying this technique to simulated concentration profiles. The corrected values of the diffusivity are in very good agreement with the results of Fick's 2nd law. Therefore, even if the prerequisites are not completely fulfilled, applying Boltzmann's integration method to concentration profiles of guest molecules in nanoporous host materials is strongly recommended because of the statistical accuracy of the received diffusivities and the feature to determine the diffusivity for a large concentration range from one sole concentration profile.

Acknowledgement

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