

Monte Carlo Simulation of Long-Range Self-Diffusion in Model Porous Membranes and Catalysts

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Industrial processes involving the use of micro-porous materials are very much dependent upon understanding the processes by which mass transport occurs in those materials. Porous catalysts and membranes are typically characterized by complex pore structures, involving pores of multiple length scales. Diffusion inside of systems of ordered nanoporous crystals (e.g., zeolites) has been studied extensively, both experimentally and computationally. However, transport in systems containing microporous particles that are separated by large meso- and/or macropores has not been sufficiently characterized. This study focuses on molecular diffusion in such systems by using dynamic Monte Carlo simulation. Simulations were conducted at a state of sorption equilibrium between the adsorbed molecules (molecules inside zeolite micropores) and molecules in the surrounding gas phase (molecules in zeolite bed mesopores and macropores). Long range diffusion in this study refers to the condition that the vast majority of diffusant molecules have traveled large distances in comparison to the size of a single zeolite crystal. The effect of varied potential barrier heights at the interface between micropores and larger pores was found to be significant in terms of its effects on the bulk diffusivity in the model zeolite system, and is reported in this study. The data was obtained using simulation parameters that are analogous to real systems of zeolites. Future comparison of the simulation data with experimental studies promises to enrich the interpretation of the experimental results.

INTRODUCTION

Diffusion is the dispersal of molecules due to thermal motion. The study of diffusion in porous media is important due to its relevance to industrial applications of chemical separations and heterogeneous catalysis. The different length scales and complex geometries of real porous media have a non-trivial effect on the diffusion of gases in and through these media.¹ Consequently, advances in industrial use of these materials are contingent upon the development of theoretical knowledge of diffusion in them. Several experimental techniques have been developed to this end. Additionally, computer modeling techniques have been used to allow researchers to explore the nature of diffusion in porous materials in ways not possible with physical experiments.

The objective of this study is to extend the modeling of diffusion inside and near a single zeolite crystal to diffusion in model membranes and catalysts consisting of many zeolite crystals separated by mesopores and macropores—namely, the construction of a model of long range diffusion in porous materials and zeolite beds. Of particular importance is maintaining the context of the microstructural complexities and their influence on the overall diffusivity of gases in the material.

BACKGROUND

Diffusion in zeolite beds and other closely related systems is a complex process involving many physical

interactions, and is generally dependent on physical conditions such as pressure, temperature, the chemical species involved, and their concentrations.² However, diffusion in these systems can be approximated by two regions with differing properties: the space inside the microporous crystals and the space surrounding these crystals.³ Equation 1 below provides a simple way to estimate the long range diffusivity (i.e. diffusivity for displacements much larger than the size of individual crystal) as the sum of the weighted averages of the diffusivities in the inter-crystalline and intracrystalline regions.

$$D_{\text{long-range}} = P_{\text{inter}}D_{\text{inter}} + P_{\text{intra}}D_{\text{intra}} \quad (1)$$

In many cases only the intercrystalline fraction is considered in the long range diffusivity because the intracrystalline term is generally smaller than the intercrystalline term.⁴ This is the case because of interactions between sorbate diffusant molecules and the pore walls lower the diffusivity of these intracrystalline diffusant molecules. This adds to the effect on the diffusivity that the confinement to the interior of the pores has. In addition to this effect, there is generally a large potential barrier for desorbing molecules at the interface of the crystal surface and the gas phase, with a much lower potential energy for molecules inside the pore structures than for molecules in the gas space between crystals. This

results in a large majority of molecules in the system being adsorbed on the pore surfaces in the crystals.

SIMULATION METHODOLOGY

Overview

Two-dimensional Monte Carlo simulations are used to model gas transport in a system of porous crystals separated by pores that have sizes comparable with the crystal size (a zeolite bed, for example). Intracrystalline diffusion is modeled as a traditional random walk algorithm, while molecular diffusion in the gas phase is modeled as a continuous motion interrupted by molecular collisions. If a diffusant molecule crosses a crystal interface, that molecule is adsorbed or desorbed with the probability P_a or P_d , respectively. The ratio of these probabilities is analogous to the interfacial potential barrier; thus it is assumed that P_d is less than P_a due to the lower potential of diffusant molecules inside of the crystals. The model potential barrier in this simulation is smaller than what might be expected in a real system of porous crystals to avoid simulation times that are prohibitively long. The ratio of these probabilities is chosen in order to achieve a desired distribution of molecules between phases; in this study the gas fraction is set to 0.25.

The initial state of the simulation is a random distribution of labeled molecules such that the concentrations in each phase match their calculated equilibrium values. The simulation then proceeds to reach a steady state where there is no net interfacial mass flux. Displacement data for each diffusant molecule is retained in order to calculate the overall diffusivity at selected times during the simulation.

Simplifying Assumptions

The simulation in this study is based upon previous modeling work done by Robert Mueller.⁵ The assumptions that form the basis for this model are laid out in a 2008 study by Krutyeva and Kärger.³ Further insight into the structure of the model was given by Dr. Sergey Vasenkov and Ph.D. candidate Robert Mueller.

Specifically, Krutyeva and Kärger show that a simple square lattice is sufficient to model diffusion in porous systems, but is still computationally expedient. There is no significant qualitative loss of generality associated with the reduction in dimensionality because of the isotropic nature of diffusion in the system. Finally, the Monte Carlo

technique implicitly assumes that particles do not interact with each other, which is physically acceptable for the case of low gas molecule concentrations.

Simulation Geometry

Figure 1 depicts the two-dimensional model system. The simulation box has length L and contains four model crystals. This simulation lattice is based upon a simulation lattice used in 2009 by Sanders and Mueller, et al.^{5,6} The crystals are arranged in the simulation box in such a way that diagonal symmetry is achieved in accordance with the assumption of an isotropic medium. Periodic boundary conditions are applied at each edge of the simulation box, resulting in a large system size in comparison to the simulation box size, as shown in Figure 1.

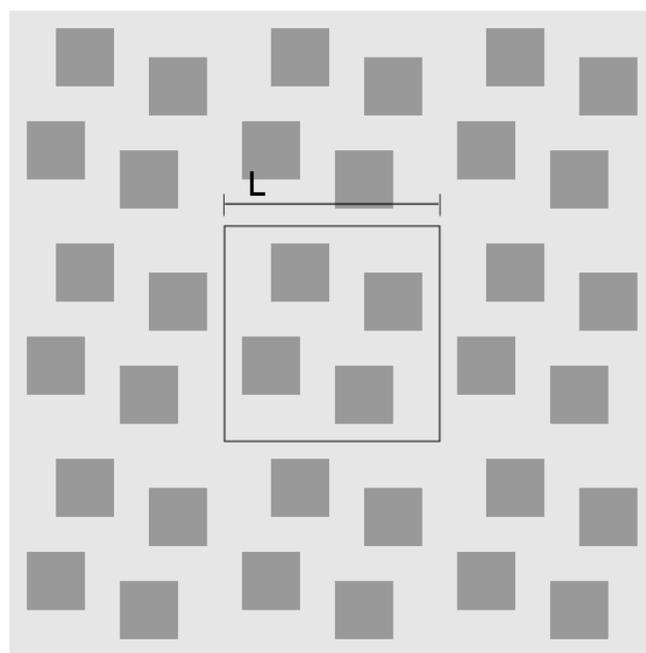


Figure 1. Schematic of the simulation box, including periodic boundary conditions

Figure 2 shows the detailed layout of the simulation box. Each crystal is a square of characteristic length $L_c = 50\lambda_c$, where λ_c is the random walk step length for molecules inside of a crystal. Each crystal is a minimum distance of $L_{sep} = 30\lambda_c$ from the next nearest crystal, and the simulation box is laid out in such a way that trajectories that might bypass many crystals are minimized.

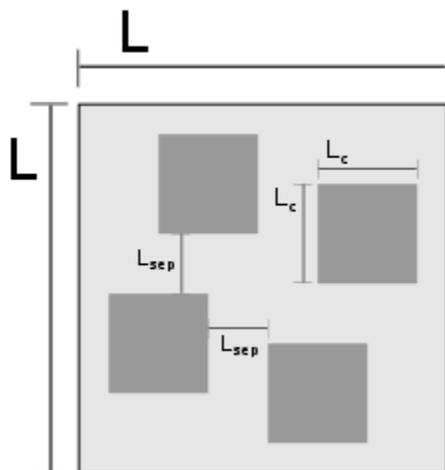


Figure 2. Simulation box details

A flux balance at the crystal external surface is used to calculate the ratio of adsorption to desorption probabilities required to achieve a desired distribution of diffusant molecules between the adsorbed and gas phases. Because of the transition between separate time and length scales at the crystal boundaries, the concentration of the diffusant molecules near the interface is different from the concentration further away from the interface. The concentration gradient was determined by a parametric fit of the simulation data and used in the flux balance to determine how to calculate the probability ratio so that a desired gas fraction is attained at steady state as follows:

$$\frac{P_a}{P_d} = \frac{\lambda_c}{f(\lambda_g)} \left(\frac{C_c}{C_g} \right) \quad (2)$$

P_a and P_d are the probabilities for molecules encountering crystal-gas interfaces to be adsorbed or to desorb, respectively. λ_c is the random walk step length for molecules inside of crystals. C_c and C_g are the desired adsorbed and gas phase bulk concentrations, respectively, and $f(\lambda_g)$ is a function of λ_g , which was determined using simulation data. Actual gas fractions achieved through the use of this relation vary by $\pm 10\%$ compared to the desired gas fraction used in the calculation (see Results and Discussion Section).

Simulation Dynamics

This simulation uses a random walk algorithm to model diffusion in a similar manner to previous versions of the simulation. The key difference between this model and previous versions is the use of separate random walk algorithms for the gas phase and the sorbate phase, as shown schematically in Figure 3. This section outlines both of these algorithms, as well as the overall dynamics of the system.

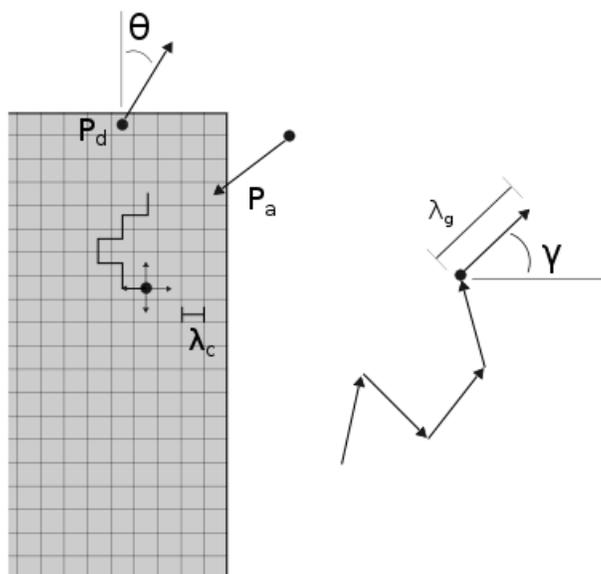


Figure 3. Schematic depiction of both random walk algorithms, as well as adsorption and desorption subroutines.

Diffusion in the zeolite micropores is modeled as a classical random walk; the simulation lattice represents the pore structure of the material. At each iteration of the simulation, sorbate molecules are randomly propagated along the simulation lattice in one of four directions, with a constant diffusion step size of λ_c , the simulation lattice constant. This behavior is illustrated in the bottom-left part of Figure 3.

In the gas phase, diffusant molecules may occupy any position, analogous to continuous movement of real gases. At each iteration of the simulation, gas-phase molecules move with a diffusion step size of λ_g at a randomly chosen angle γ with respect to the simulation lattice coordinate, as is shown in Figure 3. This diffusion step is roughly analogous to a mean free path, and is set in order to achieve the desired gas phase diffusivity. This modified random walk algorithm for the gas phase diffusant molecules affords a more realistic model of diffusion at the same time that it reduces the required number of computations in comparison with the use of the classical random walk algorithm. In prior studies, the same random walk was used for gas molecules as for sorbate molecules, requiring ten calls to the random number generator per gas molecule for each iteration. The modified random walk algorithm reduces this to a single call to the random number generator per gas molecule for each iteration, allowing more efficient modeling and larger gas fractions to be studied.

In the overview of the methods, it is mentioned that the interfacial potential barrier is modeled by probabilities that sorbate or gas molecules that encounter a crystal external

surface will desorb or be adsorbed, respectively. These probabilities are set in such a way that the desired concentration ratio is achieved. A random number is generated such that $0 \leq x \leq 1$, and if x is greater than the probability for adsorption or desorption, then the adsorption or desorption event is rejected. Rejected desorption events are handled by simply subjecting the molecule to the sorbate random walk algorithm again. Rejected adsorption events are handled by reflection from the surface according to a cosine-squared distribution, calculated according⁷ to Equation 3:

$$\theta = \arcsin(\sqrt{x}) \quad (3)$$

where θ is an angle w.r.t. the normal and x is a randomly generated number such that $0 \leq x \leq 1$. Generally, gas molecules only travel a fraction of λ_g when they encounter a crystal surface and are reflected; they travel the remaining portion of λ_g in the reflected direction described by the angle theta. Molecules that desorb are also processed according to the cosine-squared distribution of angles, and are propagated for the entire distance λ_g . Finally, gas molecules that are adsorbed do so at the nearest simulation lattice point to the intersection with the crystal surface interface. Molecules that adsorb are then carried one lattice step (λ_c) towards the interior of the

crystal in accordance with the high potential barrier at the crystal surface.

Initial Conditions

The system is initialized in a state close to the expected equilibrium distribution of molecules between phases. Molecules are randomly distributed in the gas phase only until the target gas phase concentration is reached, at which point the remaining molecules are randomly distributed in each of the four simulation box crystals. For most of the simulation runs in this study, the ratio of adsorbed molecules to gas-phase molecules is 3 to 1.

In Mueller's simulations, molecules that are originally assigned in crystals are labeled as such, in analogy to tracer exchange experiments.⁵ The particular crystal into which a given molecule is assigned (simulation time $\tau=200k$) is termed the parent of that molecule. These tracer exchange features are preserved in this study, and in Section 4 will be used to validate the modifications that have been made to the model.

Summary of Simulation Parameters

Table 1 quantifies the simulation geometry and other model parameters that were used in obtaining the results presented in the next section.

Table 1. Summary of Simulation Parameters

Simulation Parameter	Symbol	Value
Crystal Mean Free Path		λ_c
Gas Phase Mean Free Path	λ_g	$3.52\lambda_c$
Simulation Lattice Length	L	$185\lambda_c$
Crystal Side Length	L_c	$50\lambda_c$
Min. Inter-crystal Distance	L_{sep}	$30\lambda_c$
Initial Number of Gas Molecules	N_g	25000
Initial Number of Adsorbed Molecules	N_c	75000
Adsorption Probability	P_a	0.01-0.75
Desorption Probability	P_d	P_d
Probability Ratio	$\frac{P_a}{P_d}$	1.10528992

RESULTS AND DISCUSSION

Overview

The main focus of this study is to elucidate the manner in which the existence of a hierarchy of pore sizes in porous materials affects the diffusion of gases on a macroscopic length scale through these materials. The results show that the diffusivity in systems of porous crystals depends on the interfacial potential between the microporous crystals and the gas phase (i.e. large pores). The simulation results are compared with the behavior given by Eq. 1 that assumes that there are no correlations between the diffusion in the adsorbed and gas phases. In analyzing the diffusivity values obtained through the system, the root mean square displacement (RMSD) is nondimensionalized by dividing by the diagonal size of an individual crystal and used as a metric for relative simulation time. It is important to note that all the results reported have primarily qualitative significance due to the impact of the simulation parameters. Because the simulation parameters do not necessarily reflect actual physical values, but rather relative models of physical

parameters, the results are also relative in nature. Despite this limitation, much insight into the nature of diffusion in systems of porous crystals may be gained through the use of this model.

Diffusivity as a Function of Potential Barrier

Figure 4 shows the dependence of overall diffusivity on the nondimensionalized Root Mean Square Displacement (RMSD) for varying potential barrier heights. In order to achieve a gas fraction of 0.25, the ratio of P_a to P_d is assigned the constant value of 1.10528992. A steady state, long range diffusion is seen as the RMSD becomes greater than the size of a single crystal. The diffusivity varies significantly with the height of the potential barrier. For a very large potential barrier (e.g. $P_a = 0.01$), the long range diffusivity is smaller than that predicted by Eq.1 where it is assumed that D_{intra} is the unrestricted diffusivity inside the crystals far away from the crystal boundaries. For small potential barriers, the long range diffusivity approaches the value of $P_{inter}D_{inter} + P_{intra}D_{intra}$ predicted by Equation 1, as shown in Figure 4.

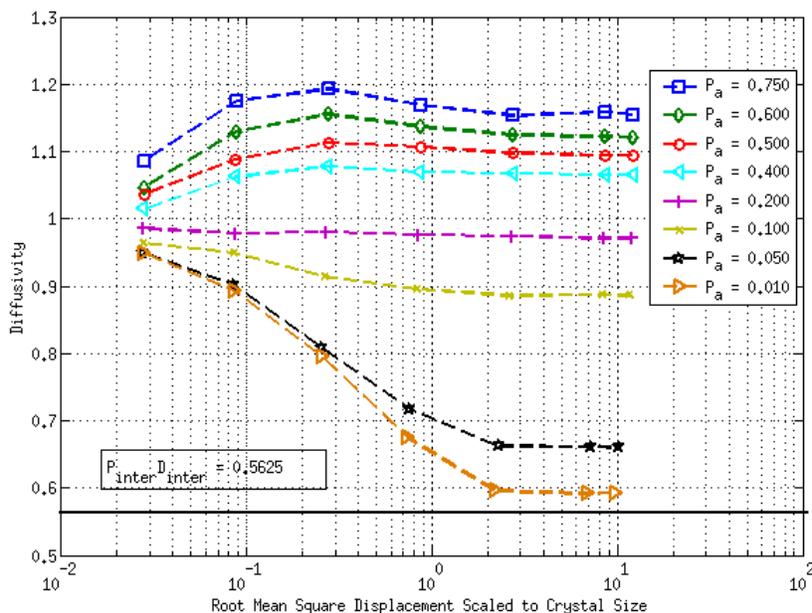


Figure 4. A Plot of Diffusivity vs. RMSD Scaled to the Size of a Crystal

Figure 5 shows more clearly the dependence of the long range diffusivity on the height of the interfacial potential barrier. The data shown here was collected at $\tau = 200k$

iterations; for reference, this corresponds to an RMSD of ten times the size of an individual crystal. There is a nonlinear relationship between the diffusivity and P_a .

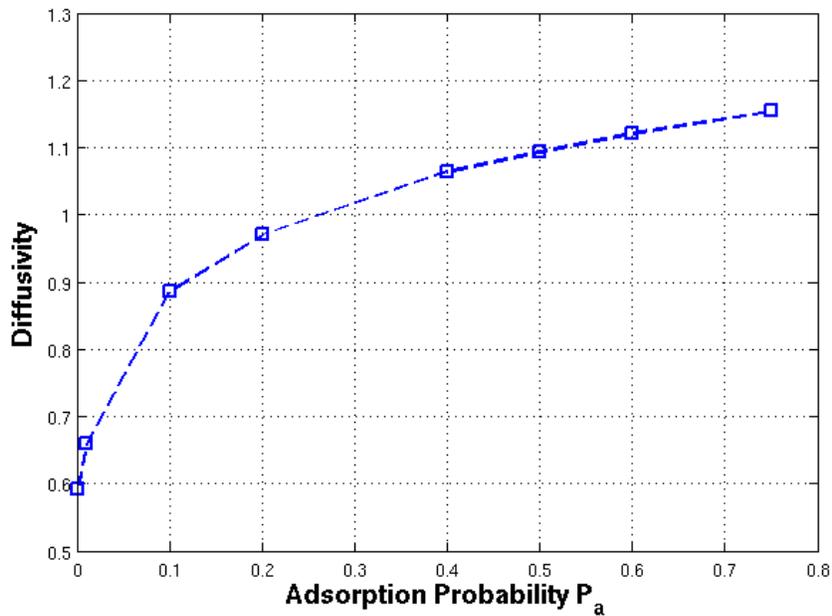


Figure 5. A Plot of Diffusivity vs. potential barrier height at simulation time $\tau=200k$

Variation in Concentration Distribution

Because the flux balance was parameterized using simulation data, as discussed in the methodology section, some variation in the gas fraction is expected for different interfacial potential barrier heights. Figure 6 shows the variation in gas concentration for the same set of potential barriers as in the previous sections. Of particular importance is that the gas fraction is inversely related to

P_a , while the long range diffusivity is directly related to P_a . Because molecules in the gas phase have a larger mean free path than those inside of crystals, a higher diffusivity is expected for larger gas fractions. That the higher gas fractions shown here correspond to lower long range diffusivities implies that these variations in the gas fraction do not account for the diffusivity trends discussed in previous sections.

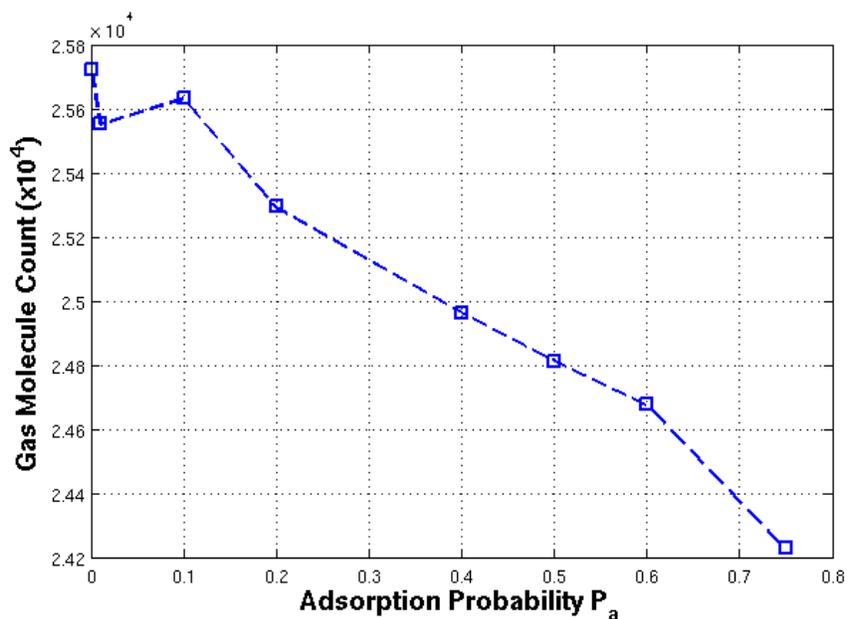


Figure 6. A Plot of Gas Phase Density vs. Potential Barrier Height

CONCLUSIONS

Monte Carlo simulations were used to gain insight into the nature of macroscale diffusion in nanoporous materials. The simulation algorithm used was designed in such a way as to provide information about the effects of the microstructure on the mass transport properties of gases in these materials.

Importantly, the long range diffusivity in the model nanoporous systems depends on the height of the interfacial potential barrier. For the case of a very large potential barrier, it is shown that the long range diffusivity approaches the value typically assumed in practice:

$$D_{\text{long-range}} = P_{\text{inter}} D_{\text{inter}}$$

For moderate and lower potential barrier heights, it is shown that the contribution of sorbate molecules to the long range diffusivity cannot be ignored, and the value of the diffusivity is more accurately described by the theoretically expected value:

$$D_{\text{long-range}} = P_{\text{inter}} D_{\text{inter}} + P_{\text{intra}} D_{\text{intra}}$$

In the future, the model that was developed during this study will continue to be used to investigate how the microstructure of porous media affects macroscale diffusion in these systems. These simulations will be used in conjunction with Pulsed Field Gradient Nuclear Magnetic Resonance techniques to gain insight into real porous media. The algorithm has been designed in such a way that the extension to modeling Knudsen-regime diffusion (very low gas-phase density) will be relatively trivial. Additionally, chemical separations or other important industrial processes could feasibly be modeled with relatively little modification to the code base.

ACKNOWLEDGEMENTS

I thank Dr. Sergey Vasenkov and Robert Mueller for the direction and support they provided for me during the three semesters that I worked with them. Dr. Vasenkov has played a key role in directing my research, and Robert has been an encouragement and an excellent resource and sounding board.

REFERENCES

1. Geier, O.; Vasenkov, S.; Kärger, J. PFG-NMR study of long range diffusion in beds of NaX zeolite: Evidence for different apparent tortuosity factors in the knudsen and bulk regimes. *Journal of Chemical Physics* **2002**, *117* (5).
2. Auerbach, S. M.; Ramanan, H. Modeling jump diffusion in zeolites: I. principles and methods. **2006**.
3. Krutyeva, M.; Kärger, J. PFG-NMR diffusivity with beds of nanoporous host particles: an assessment of mass transfer in compartmented two-phase systems. *Langmuir* **2008**, *24*, 10474–10479.
4. Papadopoulos, G. K.; Theodorou, D. N.; Vasenkov, S.; Kärger, J. Mesoscopic simulations of the diffusivity of ethane in beds of NaX zeolite crystals: Comparison with PFG-NMR measurements. *Journal of Chemical Physics* **2007**, *126* (9).
5. Mueller, R. Dynamic monte carlo simulation of self-diffusion in zeolite beds: A study of desorption and re-adsorption of tracer molecules. **2009**.
6. Sanders, M.; Mueller, R.; Menjoge, A.; Vasenkov, S. Pulsed field gradient nuclear magnetic resonance study of time-dependent diffusion and exchange of lipids in planar-supported lipid bilayers. *The Journal of Physical Chemistry B* **2009**, *113* (43), 14355–14364.
7. Greenwood, J. The correct and incorrect generation of a cosine distribution of scattered particles for monte-carlo modeling of vacuum systems. *Vacuum* **2002**, *67*, 217–222.