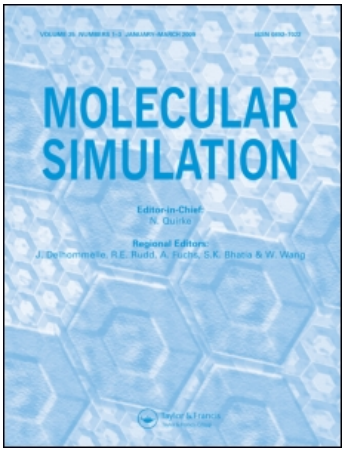

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Numerical evidence for a thermal driving force during adsorption of butane in silicalite

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Numerical evidence for a thermal driving force during adsorption of butane in silicalite

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The transport properties of nano-porous materials determine their applicability, e.g. as separators or catalysts (J. Kärger, D. Ruthven. *Diffusion in zeolites*, Wiley, New York (1991); L.V.C. Rees, D. Shen. Adsorption of gases in zeolite molecular sieves. In *Introduction to Zeolite Science and Practice, Studies in surface science and catalysis*, H.V.C. van Bekkum, E.M. Flanigen, P.A. Jacobs, J.C. Jansen (Eds.), vol. 137, pp. 579–631, Elsevier, Amsterdam (2001)). Adsorption in zeolites is explained as a two-step process; adsorption to the external crystal surface and subsequent intra-crystalline diffusion (R. M. Barrer. Porous crystal membranes. *J. Chem. Soc. Faraday Trans.*, **86**, 1123 (1990)). Both steps have been considered to be isothermal (P. Kortunov, S. Vasenkov, C. Chmelik, J. Kärger, D. Ruthven, J. Wloch. Influence of defects on the external crystal surface on molecular uptake into MFI-type zeolites. *Chem. Mater.*, **16**, 3552 (2004); J. Kärger. Measurements of diffusion in zeolites—a never ending challenge? *Adsorption*, **9**, 29 (2003)). Here we show, using non-equilibrium molecular dynamics simulations of *n*-butane in silicalite (J.M. Simon, A. Decrette, J.P. Bellat, J.M. Salazar. Kinetics of adsorption of *n*-butane on an aggregate of silicalite by transient non-equilibrium molecular dynamics. *Mol. Simul.*, **30**, 621 (2004)) that a significant temperature change accompanies adsorption and intra-crystalline transport, and leads to a significant varying thermal driving force across the crystal surface, in agreement with the proposition of Ruthven *et al.* (D.M. Ruthven, L.K. Lee. Kinetics of nonisothermal sorption: systems with bed diffusion control. *AICHE J.*, **27**, 654 (1981)). The butane flux into the crystal is caused in the first stage by a chemical potential difference. In the second stage the temperature of the zeolite decreases due to a thermal force across the surface. This slow reduction in the zeolite temperature induces a small butane uptake, that may help explain why equilibrium techniques give larger diffusion coefficients than non-equilibrium techniques (J. Kärger. Measurements of diffusion in zeolites—a never ending challenge? *Adsorption*, **9**, 29 (2003)). Descriptions of transport in nano-porous materials (J. Kärger, D. Ruthven. *Diffusion in zeolites*, Wiley, New York (1991); R. Krishna, J. A. Wesselingh. The Maxwell–Stefan approach to mass transfer. *Chem. Eng. Sci.*, **52**, 861 (1997)) need to include a thermal driving force.

Keywords: Zeolite; Non-equilibrium molecular dynamics; Kinetics of adsorption; Isothermal adsorption

The resistance to transport of molecules at the external surface is believed to be important for adsorption of gases on nanoporous zeolites. This has been documented by experiments [2,6,9] and simulations [7–9]. The surface external resistance has been attributed to the crossing of a potential barrier [1], or to the probability to stick to the surface [6,7]. According to Ruthven [5] the temperature rise that accompanies the strongly exothermic adsorption of small molecules, can influence the kinetics of adsorption. Misinterpretation of experiments is then also possible, see Refs. [10,11] and references therein.

The aim of this paper is to add evidence in support of Ruthven *et al.* [5], and show that a thermal driving force must be taken into account in descriptions of transport of small molecules in nano-porous materials. We have chosen a simple well-known process for demonstration, namely adsorption of *n*-butane in a silicalite membrane.

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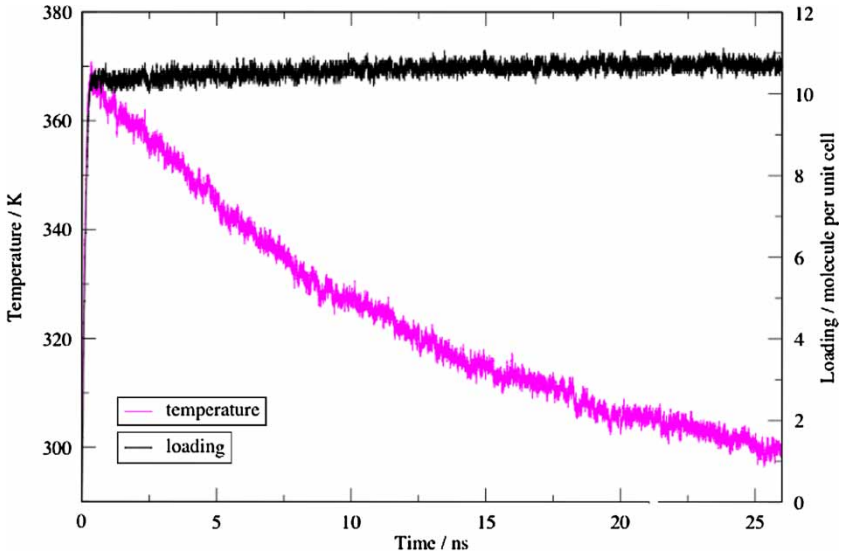

Figure 1. (a) Adsorption of *n*-butane molecules into silicalite. Loading as a function of time. (b) The average temperature of the whole silicalite during this adsorption. The gas phase at zero time contains 250 molecules and has a temperature of 300 K.

A silicalite membrane of thickness 6 nm (3 unit cells), composed of 18 Pnma orthorhombic crystalline unit cells [12], was placed in the centre of a symmetrical box of length 36 nm. The cross-sectional area of the box and of the membrane was 4×4 (nm)^2. The external surfaces were flat and normal to the straight channels. The membrane was build from the crystalline data [12] and no additional bond was added to maintain the coordinance of the atoms located at the external surface. The ends of the box were filled with 250 molecules of gaseous *n*-butane. The crystal was modelled with a flexible atomic model, allowing for stretching and bending of bonds. Butane was described using the united atom model, where the methyl and the methylene groups are considered as one centre of force. Details on the model and the potential can be found in reference [4]. The non-equilibrium state of the system was simulated using a transient non-equilibrium molecular dynamics simulation technique [4]. Periodic boundary conditions were used. Standard procedures were used to integrate Newton's equation of motion for all particles (the velocity Verlet algorithm) using a time step of 0.001 ps over 25×10^6 time steps.

Before the experiment, the gas and the membrane were thermostatted to 300 K without being in contact. At time $t = 0$, contact was made between the phases, the initial pressure was 21 bar. Butane was adsorbed and the temperature of the silicalite was recorded. A simple velocity rescaling thermostat was always on in the gas phase at the boundaries of the simulation box [4]. This situation mimics a real uptake-experiment. In a real experiment, the crystal may also have contact with a container, which can act as a heat sink. In the present case, heat can only accumulate in the crystal, and subsequently flow to the gas phase where it is removed by the thermostat.

The adsorption was followed about 25 ns. At that time the uptake was constant, and the temperature of the whole system was again 300 K. On the average 10.3 molecules per unit cell were adsorbed at equilibrium pressure of 2.3 bar. This gave results in very good agreement with previous results [13]. The total number of molecules entering the membrane from the gas phase is shown as a function of time in figure 1(a). The figure shows that the process has two stages, a rapid one where about 95% of the systems capacity for *n*-butane is filled in 0.2 ns, and a slow stage that completes the loading in about 25 ns.

Silicalite is known as a good heat conductor [20]. We therefore computed the temperature of the whole crystal from the average kinetic energy of all atoms in the crystal and of the *n*-butane inside the crystal. The results in figure1(b) show that the rapid uptake accompanied by a strong rise in temperature from 300 to 370 K, while the slow, small uptake is accompanied by an exponential-like decline in temperature back to 300 K.

The results must be understood on the basis of diffusion and thermal conduction. Radiation of heat from the crystal to the gas phase [2] can be neglected on the present time scale. The large chemical driving force for uptake at time $t = 0$, explains the rapid uptake in figure 1(b), and a large diffusion coefficient. The large enthalpy of adsorption, $\Delta H = -67$ kJ/mol, explains the accompanying temperature rise, ΔT, in the crystal. The heat capacity of the crystal per unit volume, C_v, was well approximated from the slope of the total energy of the membrane as a function of the crystal temperature in the second stage of the loading:

$$C_v = \frac{\partial E_{\text{memb}}}{V_{\text{zeo}} \partial T} \tag{1}$$

Here V_{zeo} is the volume of the zeolite membrane, C_v is 1.49×10^6 J/K m^3. This value agrees with previous experimental results [18], 1.38×10^6 J/K m^3. The diffusion coefficient for the external surface layer is $D^{\text{s}} = (d^{\text{s}})^2/2\tau_l = 2 \times 10^{-9}$ m^2/s, with a surface thickness d^{s} of about 1 nm and a relaxation time $\tau_l = 250 \pm 20$ ps. The thermal force between the external

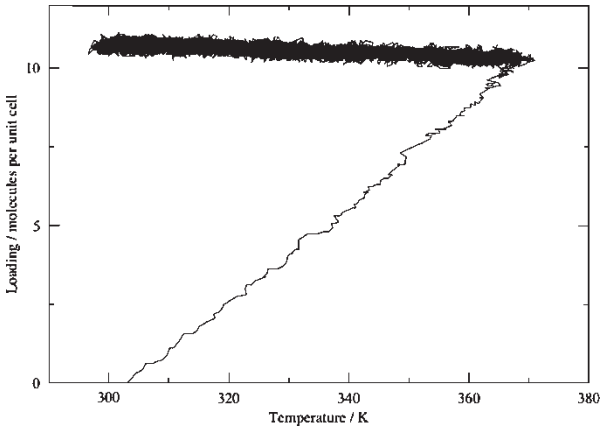

Figure 2. Adsorption of *n*-butane as a function of the average membrane temperature. The lower part of the figure represents the initial stage of the uptake, while the upper part gives results for the second stage of the uptake.

surface and the gas drives a heat flux out of the crystal:

$$J'_q = -\lambda^s \frac{\Delta T}{d^s} \tag{2}$$

The thermal driving force decreases slowly in the second stage, with a relaxation time $\tau_2 = 10 \pm 2$ ns. In this period, the loading increases slowly. Diffusion seems to be slow, a value of 7×10^{-11} m^2/s can be calculated from τ_2, but diffusion is not the rate-limiting process! The thermal conductivity is $\lambda^s = C_v(d^z d^s)/2\tau_2 = 4.5 \times 10^{-4}$ W/K m, where we have taken $d^z = 6$ nm as the thickness of the crystal. This is about 30 times smaller than the value of the gas, confirming that the surface is rate-limiting for heat transfer. The chemical potential of butane depends on the temperature however. As the temperature decreases, the chemical potential of butane goes down, leading to a corresponding influx of butane. The concentration increases linearly with the temperature decrease via this equilibrium relation, see figure 2.

These events may shed new light on experimental results for diffusion coefficients. Such coefficients have been measured for various molecules by equilibrium techniques, like nuclear magnetic resonance, quasi-elastic neutron scattering or tracer techniques, and by non-equilibrium techniques, like adsorption/desorption techniques or single crystal permeation studies [3]. Results for the same system may differ by orders of magnitude. Reasoning that the thermal force may limit diffusion like explained above, coefficients from non-equilibrium techniques may appear to be smaller than those obtained by equilibrium techniques. This is indeed found [3]. Our finding agrees with previous analytical interpretations [5,10,11,16], it is typical for transport in nano-porous materials where significant heats of adsorption exist and where the characteristic time for intra-crystalline diffusion is small in comparison with the characteristic times of heat dissipation. The finding may have a bearing on design of processes for multi-component separation, like pervaporation, membrane permeation and heterogeneous catalysis. We conclude that a thermal force must be used to describe the coupled transports of heat and mass transfer and chemical reactions in such cases [17].

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References

[1] R.M. Barrer. Porous crystal membranes. *J. Chem. Soc. Faraday Trans.*, **86**, 1123 (1990).
[2] P. Kortunov, S. Vasenkov, C. Chmelik, J. Kärger, D. Ruthven, J. Wloch. Influence of defects on the external crystal surface on molecular uptake into MFI-type zeolites. *Chem. Mater.*, **16**, 3552 (2004).
[3] J. Kärger. Measurements of diffusion in zeolites—a never ending challenge? *Adsorption*, **9**, 29 (2003).
[4] J.M. Simon, A. Decrette, J.P. Bellat, J.M. Salazar. Kinetics of adsorption of *n*-butane on an aggregate of silicalite by transient non-equilibrium molecular dynamics. *Mol. Simul.*, **30**, 621 (2004).
[5] D.M. Ruthven, L.K. Lee. Kinetics of nonisothermal sorption: systems with bed diffusion control. *AICHE J.*, **27**, 654 (1981).
[6] A. Schüring, S. Vasenkov, S. Fritszche. Influence of boundaries of nanoporous crystals on molecular exchange under the conditions of single-file diffusion. *J Phys Chem B*, **109**, 16711 (2005).
[7] J.M. Simon, J.P. Bellat, S. Vasenkov, J. Kärger. Sticking probability on zeolites. *J. Phys. Chem. B*, **109**, 13523 (2005).
[8] M.G. Ahunbay, R.J. Elliott, O. Talu. Effect of surface resistances on the diffusion of binary mixtures in the silicalite single crystal membrane. *J. Phys. Chem. B*, **109**, 923 (2005).
[9] D.A. Newsome, D.S. Sholl. Predictive assesment of surface resistances in zeolite membranes using atomically detailed models. *J. Phys. Chem. B*, **109**, 7237 (2005).
[10] J.A.C. Silva, F.A.D. Silva, A.E. Rodrigues. An analytical solution for the analysis of zero-length-column experiments with heat effects. *Ind. Eng. Chem. Res.*, **40**, 3697 (2001).
[11] S. Brandani, C. Calvacante, A. Guimarães, D. Ruthven. Heat effects in ZLC experiments. *Adsorption*, **4**, 275 (1998).
[12] H. van Koningsveld, H. van Bekkum, J.C. Jansen. On the location and disorder of the tetrapropylammonium (TPA) ion in zeolite ZSM-5 with improved framework accuracy. *Acta Crystallogr.*, **B43**, 127 (1987).
[13] T.J.H. Vlugt, R. Krishna, B. Smit. Molecular simulations of adsorption isotherms for linear and branched alkanes and their mixtures in silicalite. *J. Phys. Chem. B*, **103**, 1102 (1999).
[14] A.M. Greenstein, S. Graham, Y.C. Hudionot, S. Nair. Thermal properties and lattice dynamics of polycrystalline MFI zeolite films. *Nanosc. Microsc. Therm.*, **10**, 321 (2006).
[15] J. Boerio-Goates, R. Stevens, B.K. Hom, B.F. Woodfield, P.M. Piccione, M.E. Davis, A. Navrotsky. Heat capacities, third-law entropies and thermodynamic functions of SiO_2 molecular sieves from $T = 0$ to 400 K. *J. Chem. Thermodyn.*, **34**, 205 (2002).
[16] D.M. Ruthven, M.F.M. Post. Diffusion in zeolite molecular sieves. In *Introduction to Zeolite Science and Practice, Studies in Surface Science and Catalysis*, H.V. van Bekkum, E.M. Flanigen, P.A. Jacobs, J.C. Jansen (Eds.), vol 137, pp. 525–577, Elsevier, Amsterdam (2001).
[17] D. Bedeaux, S. Kjelstrup, L. Zhu, G. Koper. Nonequilibrium thermodynamics—A tool to describe heterogeneous catalysis. *Phys. Chem. Chem. Phys.*, **8**, 1 (2006).