Supporting Material to: The permeation of methane molecules through silicalite–1 surfaces

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1 Preventing a drift motion of the membrane

Because of the creation and deletion of particles in the bath region the total momentum of the system is not conserved. In order to prevent a drift of the whole membrane as a consequence of the irregular collisions with the methane molecules an additional potential is used that yields an elastic bond between the center of mass of the membrane and its position at the beginning of the simulation. This will disturb the system less than the frequently used total fixing of some of the lattice atoms to their initial positions.

The additional potential is

$$U_{\text{fix}} = \frac{k_{\text{fix}}}{2}(\vec{r}_S - \vec{r}_{S0})^2 \qquad \vec{r}_S = \frac{\sum m_i \vec{r}_i}{M_z} \qquad M_z = \sum m_i. \tag{1}$$

$\vec{r}_S$ is the position of the center of mass of the membrane at a given time and $\vec{r}_{S0}$ is the initial value of $\vec{r}_S$. The summation runs over the lattice atoms. M_z is the total mass of the lattice (membrane). Hence, the force on a lattice atom i as a consequence of this potential is

$$\vec{F}_i = -\frac{k_{\text{fix}} m_i}{M_z}(\vec{r}_S - \vec{r}_{S0}). \tag{2}$$

Thus, the force needed to prevent the drift is distributed over all lattice atoms and this force is weak because M_z is of the order of $10^3 m_i$. We have chosen k_{fix}=100 kJ/(mol·A).

2 Grand Canonical MD within the Control Volume

During the simulation the average number of particles within the control volume is controlled by Grand Canonical MD. During the first 10,000 MD steps particle insertion and removal is probed every 10 steps and for the remaining part of the run (typically 5-15 million steps) this is done every 100 steps.

First a site for the particle is chosen randomly in the Control Volume and the probability for accepting the insertion of an additional methane molecule is [**?**]

$$p = \min\left\{1, \frac{Z}{N_c+1}\exp\left(+\ln\frac{V_c}{\Lambda^3} - \frac{\Delta U}{k_B T}\right)\right\} \qquad Z = \exp\left(\frac{\mu}{k_B T}\right). \qquad (3)$$

where μ is the chemical potential. N_c is the number of particles which are at that moment inside the Control Volume (before the insertion) and V_c is the size of the Control Volume. ΔU is the change in the potential energy resulting from the particle insertion. Λ is the de Broglie wavelength.

If the insertion is accepted then the velocity components of the new particle are chosen randomly from the Maxwell–Boltzmann distribution at the given temperature.

For the removal of one of the particles that are within the control volume one of them is chosen randomly. The probability for the removal is

$$p = \min\left\{1, N_c Z^{-1} \exp\left(-\ln\frac{V_c}{\Lambda^3} - \frac{\Delta U}{k_B T}\right)\right\}. \tag{4}$$

Here N_c ist the number of particles before removing the particle in question.

Z is an input parameter that controls the average number of particles inside the Control Volume. In the present case it is chosen in such a way that thus number is about 10. This is achieved with $Z\Lambda^3/V_c = 10.0$.

The temperature in the Control Volume is kept constant by velocity rescaling. The gas phase and the zeolite membrane, including the guest molecules, are not thermostated.

References

[1] Allen, M. P.; Tildesley, D. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1989.