Development of nonequilibrium thermodynamics theory using molecular dynamics simulations

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Nonequilibrium molecular dynamics simulations was set up in our group in the early 1990'ies to help explain experimental results for transport coefficients and to answer questions arising in theory developments, see [1] for a review. In the development of nonequilibrium thermodynamics theory for heterogeneous systems [2], this technique in combination with equilibrium simulation techniques like Monte Carlo methods, has proven indispensable. The lecture will present evidence obtained over the years for validity of basic assumptions in Nonequilibrium thermodynamic theory, namely

- the assumption of local equilibrium,
- the assumption of linear, homogeneous flux-force relations
- the symmetry of the set of transport equations (Onsager symmetry relations)

Results will be shown that enable us to use this thermodynamic theory in systems exposed to external fields with magnitude larger than those common in the laboratory, in industry, or in nature. Local equilibrium holds e.g. in systems that contain as few as 10 particles in the stationary state. The evidence is encouraging for the possibility to obtain a dynamic description with basis in the second law of thermodynamics, also for processes on the nanoscale where fields are strong, like in biology, in nanomachines, reactions in flames, phase transitions, nucleation or heterogenous catalysis.

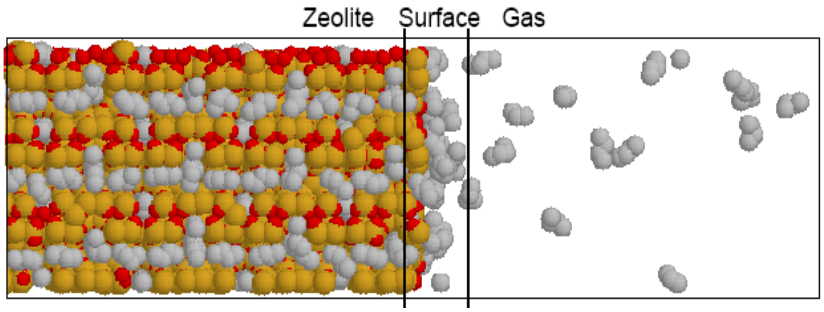

Fig.1.A box to simulate the rate of gas and heat absorption in zeolite

The lecture will present simulation results for the common liquid-vapor phase transition, the adsorption into a typical zeolite (illustrated in Fig.1), and for a chemical reaction in a flame, and show that the nonequilibrium thermodynamic description is valid and also that this description, which is rooted in the second law, gives new insight.

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[1] B. Hafskjold, *Thermal Nonequilibrium Phenomena in Fluid Mixtures*, W. Kohler and S. Wiegand, eds. Computer Simulations of Thermal Diffusion in Binary Fluid Mixtures, Lecture Notes in Physics, Springer, Berlin 2002
[1] S. Kjelstrup and D. Bedeaux, *Non-equilibrium thermodynamics for heterogeneous systems*, Series on Advances in Statistical Mechanics, Vol. 16, World Scientific, Singapore, 2008