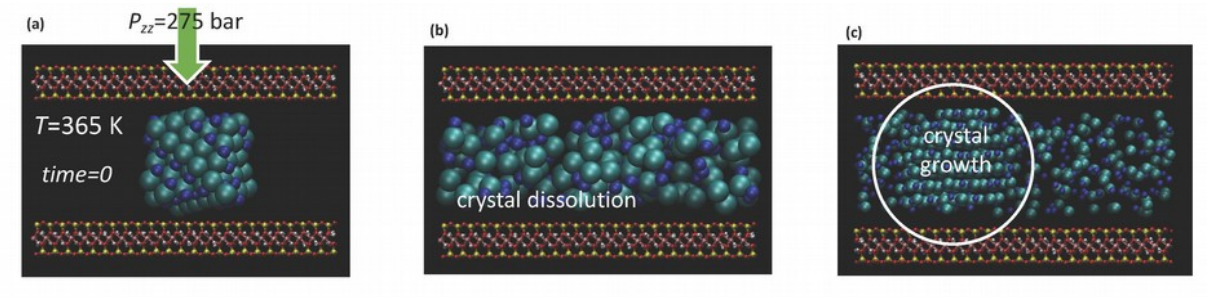
# Modeling aqueous dissolution of sodium chloride in clays at thermodynamic conditions of hydraulic fracturing by molecular dynamics simulations

Martin Svoboda[1,2,*] and Martin Lísal[1,2]

[1]*Laboratory of Aerosols Chemistry and Physics, Institute of Chemical Process Fundamentals of the CAS, v. v. i., Prague, Czech Republic*
[2]*Department of Physics, Faculty of Science, J. E. Purkinje University, Ústí nad Labem, Czech Republic*

To address a high salinity of flow-back water during hydraulic fracturing we use molecular dynamics simulations and study the dissolution of a cubic NaCl nanocrystal immersed in aqueous NaCl solutions of varying concentration, confined in clay pores of the width comparable to the crystal size. We consider a typical shale gas reservoir condition of 365 K and 275 bar, and we represent the clay pores as pyrophyllite and Na-montmorillonite (MMT) slits. We employ the Joung-Cheatham model for ions and SPC/E model for water [1], and CLAYFF [2] for the MMTs. The pressure is applied along the normal direction and slit width varies from about 23 to 28 Å when the salt concentration increased from zero to a high concentration. By varying the salt concentration, we observe two scenarios. First, the crystal dissolves and its dissolution time increases with increasing the salt concentration. We describe dissolution process in terms of number of ions in the crystal and the crystal shape. After the crystal dissolution, we characterise an equilibrium confined system of water molecules and dissolved ions by evaluating the structure, orientation and in-plane diffusion of water and ions, along with ion conductivities. Second, when the salt concentrations reach a saturation threshold the crystal growths and attains a new equilibrium size. The crystal becomes in equilibrium with a surrounding saturated solution.




(a) NaCl nanocrystal immersed in an aqueous NaCl solution (only nanocrystal shown). (b) Crystal dissolution. (c) Crystal growth.

[1] Joung I. S., Cheatham T. E. (2008). Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. J. Phys. Chem. B 112, 9020.

[2] Cygan R. T., Liang J.-J., Kalinichev A. G. (2004). Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. J. Phys. Chem. B 108, 1255.