Fluid in mineral interfaces—molecular simulations of structure and diffusion

D. K. Dysthe[1]
Fluid Rock Interaction Group, Departments of Geology and Physics, University of Oslo, Norway

F. Renard[1]
LGIT-CNRS-Observatoire, Université Joseph Fourier, France

F. Porcheron and B. Rousseau
Laboratoire de Chimie Physique (LCP), Université Paris-Sud, France

Received 20 March 2001; revised 15 October 2001; accepted 1 November 2001; published 10 April 2002.

[1] We study the effect of burial depth on thermodynamics and transport properties of fluids confined between mineral surfaces. The solvation curve and diffusion coefficients of fluid films confined between mineral surfaces have been obtained for different states of stress and temperature using Grand Canonical Monte Carlo and molecular dynamics simulations. Our results indicate that the mass transport coefficient (film thickness times diffusion coefficient) of the thin films of fluids trapped at grain contacts decrease by a factor 40 from 1 km to 3 km and 10 km. This effect has strong implications on the rates at which mechano-chemical processes of deformation (e.g. pressure solution) occur in the upper crust. *INDEX TERMS:* 3675 Mineralogy and Petrology: Sedimentary petrology; 3947 Mineral Physics: Surfaces and interfaces; 5139 Physical Properties of Rocks: Transport properties; 8045 Structural Geology: Role of fluids

1. Introduction

[2] Recent new experimental techniques applied to mineral interfaces have shown that interfacial properties and mechanisms are critical for understanding geodynamic processes, petrologic reactions, transport properties, and resource recovery. Organic molecules are present in sedimentary basins and water is almost omnipresent at mineral interfaces in the earths crust. The interfacial fluids play an important role in transport and reactions at the grain contacts in rocks [*Hickman and Evans*, 1991; *Israelachvili*, 1991].

[3] Pressure solution creep has for a long time been considered as an important ductile rock deformation mechanism during diagenesis of sedimentary rocks. Aggregates of mineral grains in sedimentary basins experience an increasing overburden pressure relative to the fluid pressure as they are buried deeper with time. It is well established that the high stress at grain contacts cause dissolution of the minerals at the grain boundary, transport of the dissolved matter *in a fluid phase* out of the grain boundary and precipitation of this material in the pore space on the less stressed faces of the grains [*Weyl*, 1959; *Rutter*, 1976].

[4] The nature of the grain-grain interface is crucial because it is the place where the dissolution of the mineral and the transport of solutes to the surrounding pore space occurs. The exact nature of the grain-grain interface is under debate, this study seeks only to study the properties of the so-called "fluid film model" [*Weyl*, 1959]. Many authors have demonstrated that a fluid film can be trapped between the sheets of minerals such as clays and micas [*Pashley and Israelachvili*, 1984] or sapphires [*Horn et al.*, 1989]. In the fluid film model for diffusion-controlled pressure solution, the thickness and transport properties (diffusion coefficient) of this film control the rate at which solutes are expelled from the stressed contact to the pore [*Renard et al.*, 1999]. Assuming a flat interface, several authors have estimated the product of the coefficient of diffusion and fluid film thickness from pressure solution experiments and found values from 10^{-18} to 10^{-21} m^3/s [*Rutter*, 1976; *Gratier and Guiguet*, 1986].

[5] Molecular simulations have already proven to be a good tool for the study of confined fluid [*Snook and van Megen*, 1980; *Schoen et al.*, 1987; *Porcheron et al.*, 1999]. A confined fluid between parallel walls exhibits periodically damped oscillations of the normal component of the stress tensor as a function of the wall separation (the so-called solvation force curve). These oscillations correspond to structural changes of the adsorbed film. In most of the studies, the simulation model consists of a monoatomic fluid (described by a Lennard-Jones potential) confined between rigid walls of like atoms. It has been shown that at solvation force repulsive peaks the fluid is solid-like and diffusion is slow [*Bordarier et al.*, 1996]. Molecular simulations of confined fluids in a geological setting have been performed on clays [*Boek et al.*, 1995; *Titiloye and Skipper*, 2000, 2001; *deCarvalho and Skipper*, 2001]. The fluid film properties in montmorillonite clay has recently been studied as a function of burial depth assuming a given constant number of molecules in the fluid films [*Titiloye and Skipper*, 2001].

[6] It is the purpose of this article to calculate fluid film properties of a fluid-mineral model as function of burial depth in the upper crust. The crude, "generic" fluid-mineral model is made to represent some properties of water–calcite. The thermodynamic ensemble is chosen to obtain fluid film thickness and number of fluid molecules as a result and not as input. By these means we intend to qualitatively study how transport in the grain contact during pressure solution changes with burial depth.

2. Simulation Method, Potential and Thermodynamic Parameters

[7] In this section we will briefly describe the methodology of the molecular simulations, how the parameters of the molecular models and the thermodynamic parameters are chosen and the scope of results.

2.1. Simulation Method

[8] Firstly, we use Grand Canonical Monte Carlo (GCMC) to calculate the equilibrium properties of a fluid film confined between two flat "mineral" surfaces. The fluid phase is in

[1]Academic year 2000–2001 at Fluid Rock Interactions Group, Centre for Advanced Study, Oslo, Norway.

0094-8276/02/2001GL013208$05.00

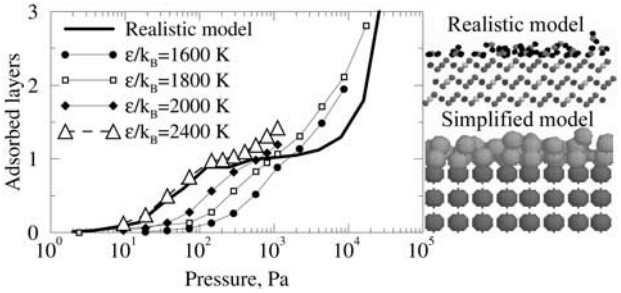

Figure 1. Left: Adsorption isotherms at 273 K of the realistic model (thick solid line) and the Lennard-Jones model with varying well depth parameter ε. One observes that the adsorption isotherm with ε/k_B = 2400K gives the best fit to the realistic potential for the first adsorbed layer. Right: Cartoons of realistic (Dreiding and TIP3P) and simplified (LJ) models of the calcite–water interface. Each $CaCO_3$ and H_2O molecule is replaced with a corresponding spherical potential.

thermodynamic equilibrium with a bulk fluid at specified chemical potential and temperature. The wall separation, that is the distance between the solid surfaces is kept constant and the mean number of fluid molecules occupying the space between the walls is calculated as well as the pressure exerted by the fluid on the mineral surfaces—the *solvation pressure*, σ_{zz}. The grand canonical and grand isostress ensembles are the only possible choices to obtain the wall separations at given overburden stress. Attempts to use the grand isostress ensemble [*Bordarier et al.*, 1996] led to fluctuations in particle number and wall separations that were too large for the simulations to converge for the large systems at 1 km.

[9] Secondly, the equilibrium configurations calculated by GCMC are used as the starting point for Molecular Dynamics (MD) simulations in the canonical ensemble to calculate diffusion coefficient of the confined fluid in the plane parallel to the walls (the *xy* plane). The simulations are performed at three different thermodynamic conditions corresponding to three different burial depths: 1, 3 and 10 km.

[10] We have used simulation cells of 38.4 × 38.4 Å in the *xy* plane with a thickness of the solid slab of 28.8 Å (which is larger than the cutoff length of the wall—fluid interaction) and a distance between the solid surfaces of 8 to 80 Å, which corresponds to a number of fluid molecules between 300 and 6500. The GCMC code has been run on Linux workstations and on an SGI Origin for up to $4 \cdot 10^6$ cycles to converge properly. The MD code has been parallelized and has been run for $2 \cdot 10^6$ timesteps on a Cray T3E on 17 to 21 processors. For the largest system this takes up to 16 hours run time.

2.2. Choice of Potential Parameters

[11] We aim at studying *qualitatively* the effect of burial depth on thermodynamic and transport properties of fluids confined between mineral surfaces. Numerical values of the thermodynamic properties like the solvation pressure depend strongly on charge distributions in the solid, the dipole moment and hydrogen bonding of water and the concentration and type of ions in the fluid. To obtain numerical values for thermodynamic properties of confined water comparable (within 10% which is state of the art in chemical engineering) to real geological systems one must use multicomponent systems with very sophisticated interatomic potential models and rough mineral surfaces. Even then, due to the number of possible complex geological situations, it is uncertain what such a simulation corresponds to. On the other hand, a recent experimental study of confined water [*Raviv et al.*, 2001] shows that confinement suppresses the formation of the highly directional H-bonded network associated with freezing. It is therefore not necessary to include H-bonding to obtain qualitatively correct trends for confined water. It has also been known for a long time that even hard sphere representation of water (as in the Enskog theory) is sufficient to describe the transport properties of both non-polar and hydrogen-bond forming fluids over large ranges of pressure and temperature [*Dymond*, 1974; *Krynicki et al.*, 1978].

[12] The rational of this study is to use simple Lennard-Jones (LJ) interatomic potentials, with parameters chosen to mimic important aspects of the real systems. The use of simple potentials allows the large simulations necessary for this study. The LJ potential is a spherical symmetric potential with two parameters: the diameter of the repulsive "core", σ, and the strength of the attractive force, or the "well depth", ε. In addition to these two parameters for each of the fluid and solid "molecules" we will have to fix the mineral structure parameters.

[13] We choose to use the 104 calcite cleavage surface as departure point for making a LJ mineral model. To simplify the structure we use a face centered cubic unit cell size a = 6.4 Å to have the same number of adsorption sites for water per unit as surface of calcite. A LJ sphere will in some sense represent a $CaCO_3$ unit in the calcite. The LJ diameter was chosen in order to fully minimize the potential energy between nearest neighbors in the crystal, giving σ_s = 4.0 Å. Figure 1 shows a realistic model compared with the simplified LJ model.

[14] The parameters for the fluid representing liquid water are obtained by a simple triple point mapping to the LJ fluid yielding σ_f = 2.9 Å and ε_f/k_B = 400 K, where k_B is the Boltzmann constant. The triple point data of LJ are taken from [*Johnson et al.*, 1993]. These parameters give diffusion coefficients of bulk fluid at 3 and 10 km depth (see Table 1) that are within 20% of experimental values for water [*Krynicki et al.*, 1978]. The remaining parameter, the well depth of the solid, ε_s can be used to adjust the cross interaction between the wall and the fluid. We want a wall—fluid interaction that is roughly correct at short range. We choose to compare the adsorption isotherm of the first adsorbed layer of water on calcite with identical GCMC simulations using realistic potential models that have been used extensively to model the water—mineral systems [*Boek et al.*, 1995]: the Dreiding [*Boek et al.*, 1996] force field for the wall and the TIP3P [*Jorgensen et al.*, 1983] model for water. Figure 1 shows the adsorption curves of the realistic potential model simulation compared with the LJ model with varying well depth parameter. The value of the cross interaction parameter modifies the pressure at which the first layer occurs on the mineral surface. The LJ well depth parameter giving the best fit to the more realistic model is therefore ε_s/k_B = 2400 K.

[15] In the simulation the grain contact is assumed to be atomically flat over a length scale much smaller than experimentally measured contact roughness [*Spiers et al.*, 1990; *denBrok and Spiers*, 1991]. During the timescale of a simulation (10 ns) it is

Table 1. Conditions in the Upper Crust at 1, 3 and 10 km Depth

Geological Conditions				Bulk Fluid Results			Confined Fluid Results		
z (km)	T (K)	σ_{zz} (MPa)	P_{fluid} (MPa)	ρ_{fluid} (kg.m^{-3})	μ_{fluid} (K)	D_{fluid} (10^{-9} m^2 s^{-1})	$S_{z,max}$ (Å)	$\bar{D}_{conf}$ (10^{-9} m^2 s^{-1})	$S_{z,max}\bar{D}_{conf}$ (10^{-19} m^3 s^{-1})
1	313	30	10	982	−4074	5.2	>80	4	320
3	373	77	30	914	−4502	9.1	11.5	0.7	8.1
10	573	250	100	663	6064	32	9.5	0.9	8.6

Temperatures, lithostatic and hydrostatic stress are computed by simple formulae given in the text, the bulk and confined fluid values are results from molecular simulations.

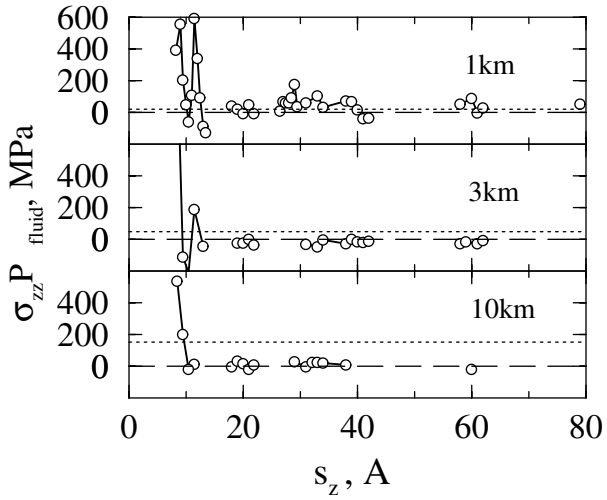

Figure 2. Solvation pressure at various burial depths. The open circles show the pressure σ_{zz} the confined fluid excerts on the mineral wall, minus the bulk fluid pressure P_{fluid} at different wall separations s_z. The dotted lines show the overburden pressure at the different burial depths. The fluid film is capable of supporting the overburden pressure where the net fluid pressure equals the overburden pressure.

valid to assume the solid as inert (no dissolution or precipitation). The effect of atomic scale roughness and solutes in the fluid phase should be included in future work.

2.3. Choice of Thermodynamic Conditions

[16] We have chosen the temperature and pressure conditions so that they correspond approximately to geological conditions at different burial depths. We ignore all variations due to history and chemistry and take a general view of a limestone (or a sandstone) from the surface downwards down to 10 km. The temperature, T, mean stress at grain contacts, σ_{zz} and pore fluid pressure, P_{fluid}, at 1, 3 and 10 km are shown in Table 1. The generic, geological parameters (stress, pore pressure and temperature) at depth chosen here are in good agreement with measurements from the German deep hole project (KTB) [*Emmerman and Lauterjung*, 1997].

3. Results

3.1. Temperature Dependence of Solvation Pressure—Melting

[17] Figure 2 shows the effective solvation pressure ($\sigma_{zz} - P_{\text{fluid}}$) of the fluid between flat surfaces as function of wall separation, s_z, at the three different crustal depths. As expected one observes an oscillatory behavior of the solvation pressure as function of wall separation. The oscillations are not regularly spaced or easily modeled theoretically due to the different parameters of the fluid and the wall models. At all three depths the effective solvation pressure oscillates above and below zero (long dashed line in Figure 2) but the amplitudes of the oscillations decrease with depth. This is thought to be an effect of the increasing temperature—the increased molecular motion disrupts the ordering into layers. This has dramatic consequences for the maximum stable wall distance at the three depths. The dotted lines in Figure 2 indicate the values of the effective overburden stress, $\sigma_{zz,o} - P_{\text{fluid}}$. The overburden stress, $\sigma_{zz,o}$, is the mean normal stress on mineral surfaces in contact at that depth. There is thermodynamic equilibrium between the fluid and the overburden when the solvation pressure equals the overburden stress. At 1 km depth the maximum equilibrium distance is larger than 80Å (due to the large number of particles when the wall separation becomes large, we have not performed simulations at larger wall separations than 80Å), whereas at 3 km it is 11.5Å and at 10 km it is 9.5Å. Even though the bulk fluid pressure increases with depth the increased temperature lowers the bulk fluid density and destroys the structuring of the confined liquid that exists at 1 km even at wall separations greater than 80Å. We do not know of any systematic study of the effect of temperature on structure and solvation pressure of confined fluids, but the results presented here indicate that a temperature change of 60°C has dramatic consequences for the solvation pressure of a confined fluid. We cannot conclude at which depth such a transition occurs for water in real mineral contacts, but we are confident that the qualitative trend is correct and important for geological processes like pressure solution. At 1 km depth the solvation pressure curve crosses the overburden pressure curve at several wall separations (see Figure 2). This indicates that there are several local thermodynamically stable wall separations. These are local equilibrium and not meta-stable separations. Which equilibrium distance a particular mineral contact "chooses" is obviously a function of its history. The history of a contact involves gradual change in fluid pressure, overburden stress and temperature as well as change in wall topography through dissolution and precipitation of the solid. This dynamic process must be studied in order to describe the probabilities of occupation of the different stable thermodynamic situations.

3.2. Mean Diffusion at Maximum Stable Wall Separation

[18] In Table 1 we have summarized equilibrium and mean self diffusion results at the three burial depths studied. We have performed MD simulations at the maximum stable wall separations, $s_{z,\max}$, and calculated the mean self diffusion coefficient, $\bar{D}_{\text{conf}}$, from the mean square displacement in the xy plane of all the fluid particles. The mean self diffusion coefficient of the confined fluid is reduced by almost a factor 6 when going from 1 km to 3 km and it hardly rises when going down to 10 km even though the temperature increases by 200 K. In the bulk fluid, on the other hand, the diffusion coefficient is doubled when going from 1 km to 3 km and it is tripled again when going to 10 km. This indicates that the mass flux for a given concentration gradient of labeled fluid molecules (which is proportional to the diffusion coefficient times the wall separation) decreases by a factor 40 when going from 1 km to 3 and 10 km. Again, we stress that the model applied is crude and that one cannot use the numbers in modeling of real applications, but we maintain that the results are qualitatively correct. The combined effect of increased temperature (leading to a collapse in confined fluid structure) and increased overburden pressure causes a collapse in maximum equilibrium distance and a lowering of the mean diffusion coefficient—all in all causing much lower transport capacity of the confined fluid at greater depth. The diffusion coefficients of solid solutes in a confined fluid will qualitatively follow the trend of the fluid self diffusion except at very small fluid film thicknesses where charged solutes are even less mobile due to the strong interaction with the mineral walls [*Titiloye and Skipper*, 2001].

4. Discussion

[19] The product of diffusion coefficient times fluid film thickness we obtain by molecular simulations drops by a factor 40 from 1 to 3 km and does not vary much between 3 and 10 km depth (around $8 \cdot 10^{-19}$ m^3/s) where pressure solution creep is known to be important. This value is in the range measured independently in pressure solution experiments [*Rutter*, 1976; *Gratier and Guiguet*, 1986]. We stress that these simulations do not give an absolute value of this parameter but its evolution with depth is captured in a realistic way. Its invariance at large depth represents two antagonistic effects on the pressure solution creep rate. On one hand, the increase of temperature should enhance diffusion at the grain

contact. On the other hand, the increase of temperature and stress induce a collapse of the water film and decreases the flux out of the contact. These two effects cancel each other. The consequence for diffusion-limited pressure solution creep in the fluid film model is that the only effect of depth on the creep rate will be on gradient of concentration between the contact and the pore (controlled by the solubility of the mineral) and not on the transport properties of the mineral interfaces which can be considered to remain constant with depth.

[20] **Acknowledgments.** The project has been supported by the Norwegian Rearch Council through the *Fluid Rock Interaction* Strategic University Program (grants 113354-420). The authors gratefully acknowledge the aid of J. Alexander in performing the realistic adsorption simulations.

References

Boek, E. S., P. V. Coveney, and N. T. Skipper, Monte carlo molecular modeling studies of hydrated Li-, Na-, and K-smectites: Understanding the role of potassium as a clay swelling inhibitor, *J. Am. Chem. Soc.*, *117*, 12,608–12,617, 1995.

Boek, E. S., P. V. Coveney, S. J. Williams, and A. S. Bains, A robust water potential parameterisation, *Mol. Sim.*, *18*, 145–154, 1996.

Bordarier, P., B. Rousseau, and A. Fuchs, Solvation force and confinement-induced phase transitions of model ultra thin films, *Molec. Sim.*, *17*, 199–215, 1996.

denBrok, S. W. J., and C. J. Spiers, Experimental-evidence for water weakening of quartzite by microcracking plus solution precipitation creep, *J. Geol. Soc.*, *148*, 541, 1991.

deCarvalho, R. J. F. L., and N. T. Skipper, Atomistic computer simulation of the clay-fluid interface in colloidal laponite, *J. Chem. Phys.*, *114*, 3727, 2001.

Dymond, J. H., Corrected Enskog theory and the transport coefficients of liquids, *J. Chem. Phys.*, *60*, 969, 1974.

Emmerman, R., and J. Lauterjung, The german continental deep drilling program KTB: Overview and major results, *J. Geophys. Research*, *102*, 18,179–18,201, 1997.

Gratier, J. P., and R. Guiguet, Experimental pressure solution-deposition on quartz grains: the crucial effect of the nature of the fluid, *Journal of Structural Geology*, *8*, 845–856, 1986.

Hickman, S. H., and B. Evans, Experimental pressure solution in halite-The effect of grain interphase boundary structure, *Journal of the Geological Society, London*, *148*, 549–560, 1991.

Horn, R. G., D. T. Smith, and W. Haller, Surface forces and viscosity of water measured between silica sheets, *Chem. Phys. Lett.*, *162*, 404–408, 1989.

Israelachvili, J. N., *Intermolecular and surfaces forces*, London: Academic Press, 1991.

Johnson, J. K., J. A. Zollweg, and K. E. Gubbins, The Lennard-Jones equation of state revisited, *Mol. Phys.*, *78*, 591–618, 1993.

Jorgensen, W. J., J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, Comparison of simple potential functions for simulating liquid water, *J. Chem. Phys.*, *79*, 926–935, 1983.

Krynicki, K., C. D. Green, and D. W. Sawyer, Pressure and temperature dependence of self-diffusion in water, *Faraday Disc. Chem. Soc.*, *66*, 199, 1978.

Pashley, R. M., and J. N. Israelachvili, Molecular layering of water in thin films between mica surfaces and its relation to hydration forces, *Journal of Colloid and Interface Science*, *101*, 510–522, 1984.

Porcheron, F., B. Rousseau, A. Fuchs, and M. Schoen, Monte carlo simulations of nano-confined n-decane films, *Phys. Chem. Chem. Phys.*, *1*, 4083, 1999.

Raviv, U., P. Laurat, and J. Klein, Fluidity of water confined to subnanometre films, *Nature*, *413*, 51, 2001.

Renard, F., P. Ortoleva, and J. P. Gratier, An integrated model for transitional pressure solution in sandstones, *Tectonophysics*, *312*, 97–115, 1999.

Rutter, E. H., The kinetics of rock deformation by pressure solution, *Philosophical Transactions of the Royal Society of London*, *283*, 203–219, 1976.

Schoen, M., D. Diestler, and J. Cushman, Fluids in micropores. i. structure of a simple classical fluid in a slit pore, *J. Chem. Phys.*, *87*, 5464, 1987.

Snook, I., and W. van Megen, Solvation forces in simple dense fluids, *J. Chem. Phys.*, *72*, 2907, 1980.

Spiers, C. J., P. M. T. M. Schutjens, R. H. Brzesowsky, C. J. Peach, J. L. Liezenberg, and H. J. Zwart, Experimental determination of constitutive parameters governing creep of rocksalt by pressure solution, *Geol. Soc. Spec. Publ.*, *54*, 215, 1990.

Titiloye, J. O., and N. T. Skipper, Computer simulation of the structure and dynamics of methane in hydrated Na-smectite clay, *Chem. Phys. Lett.*, *329*, 23, 2000.

Titiloye, J. O., and N. T. Skipper, Molecular dynamics simulation of methane in sodium montmorillonite clay hydrates at elevated pressures and temperatures, *Mol. Phys.*, *99*, 899, 2001.

Weyl, P. K., Pressure solution and the force of crystallization—a phenomenological theory, *Journal of Geophysical Research*, *69*, 2001–2025, 1959.

D. K. Dysthe, Fluid Rock Interactions Group, Departments of Physics and Geology, University of Oslo, P.O. Box 1048 Blindern, N-0316 Oslo, Norway. (d.k.dysthe@fys.uio.no)

F. Renard, LGIT-CNRS-Observatoire, Université Joseph Fourier, Grenoble F-38041, France. (Francois.Renard@obs.ujf-grenoble.fr)

F. Porcheron and B. Rousseau, Laboratoire de Chimie Physique (LCP), Bâtiment 349, Université Paris-Sud, 91405 Orsay Cedex, France. (fabien.porcheron@lcp.u-psud.fr; bernard.rousseau@lcp.u-psud.fr)