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► **To cite this version:**

Matthieu Vandamme, Zdeněk Pavel Bažant, Sinan Keten. Creep of lubricated layered nano-porous solids and application to cementitious materials. *Journal of Nanomechanics and Micromechanics*, 2015, 5 (4), pp.8. <10.1061/(ASCE)NM.2153-5477.0000102>. <hal-01273134>

HAL Id: hal-01273134

<https://hal.science/hal-01273134v1>

Submitted on 10 May 2019

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1 Creep of Lubricated Layered Nano-Porous
2 Solids and Application To Cementitious
3 Materials

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16 March 18, 2015

17 **Abstract**

18 A variety of geomaterials, such as cementitious or clay-based ma-
19 terials, has on the nano-scale a layered microstructure which can con-
20 tain fluid in its nano-porous space. The creep of such nano-scale basic
21 units is what causes the macroscopic creep. Here, we study one nano-
22 pore whose walls consist of two parallel infinite solid layers interacting

23 through Lennard-Jones potential. We evaluate numerically the energy
24 barriers that such a system needs to overcome in order for the two solid
25 layers to slide over each other, and show how this sliding depends on
26 the longitudinal and transverse forces applied to the layers. The en-
27 ergy barriers translate into a dependence of the apparent viscosity of
28 the system on the disjoining pressure, in a manner consistent with the
29 microprestress theory. This result makes it possible to explain why
30 the long-time creep of cementitious materials is logarithmic. We then
31 consider experimental data on how the long-term logarithmic creep of
32 cementitious materials depends on the temperature and relative hu-
33 midity. Our model can capture the observed dependencies if we take
34 into account not only the energy barriers induced by the interactions
35 between layers, but also the influence of the interlayer fluid, which is
36 water in the case of cementitious materials. We model this fluid as a
37 continuum with the same properties as the bulk fluid.

38 **Introduction**

39 All geomaterials, whether man-made, e.g., cementitious materials in general,
40 or natural, clay-based materials, exhibit creep, i.e., slow deformation over
41 time under the action of sustained mechanical stress. The creep occurs at
42 a rate that can be detrimental to the lifespan of concrete structures and
43 structures on clay foundations [Bažant *et al.* 2011; Puzrin *et al.* 2010]. Ce-
44 mentitious and clay-based materials have in common a phase that confers to

45 them most of their viscous properties, is nano-porous and layered.

46 Indeed, the matrix of regular Portland cement paste is made of calcium
47 silicate hydrates (also called C-S-H) which, although spatially variable in
48 both structure and composition [Richardson 1999], consist of more or less
49 ordered stacks of calcium silicate layers, each of which is made of a Ca-O
50 sheet covalently bonded with silicate chains [Richardson 2008; Pellenq *et al.*
51 2009]. Between those solid calcium silicate layers, one finds a few molecular
52 layers of water.

53 By contrast, as their name suggests, the minerals in clay-based materials
54 are phyllosilicates made of stacks of layers combining silicate tetrahedra with
55 aluminum octahedra [Meunier 2005]. Again, between those solid layers, one
56 finds a few molecular layers of water. Thus the cement-based and clay-based
57 materials share a layered nano-structure which contains interlayer water.

58 Because the spacing of the adjacent solid layers is on the order of only a
59 nanometer, the clay and C-S-H are subjected to strong disjoining pressures.
60 At the scale of an individual slit nano-pore, the disjoining pressures can lead
61 to swelling or shrinkage during sorption or desorption, and can be not only
62 positive (compression) but also negative (tension). The sign of the disjoining
63 pressure is affected by the ratio of nano-pore width to the number molecular
64 layers of the interlayer fluid in the nano-pore [Ustinov & Do 2006; Bažant &
65 Bazant 2012].

66 However, when averaged over a distribution of pore sizes in a disordered
67 nano-porous solid (e.g., even in ideal one-dimensional nano-porous solids

68 [Brochard *et al.* 2012]), one observes during sorption only swelling: In a
69 disordered nano-porous solid, the representative disjoining pressure is posi-
70 tive (i.e., compressive), inducing tensile stresses in the solid microstructure
71 of material (this also means that during desorption one observes only shrink-
72 age). At the macroscopic scale of material, those tensile stresses induced by
73 disjoining pressure and adsorption can reach several dozens of MPa [Espinoza
74 *et al.* 2014]. Locally, those tensile stresses can even be greater, exceeding a
75 hundred of MPa [Bažant 1972].

76 For both cementitious materials and clay-based materials, various kinetics
77 of creep can be identified. In cementitious materials, a short-term creep
78 kinetics, usually associated with local reorganization of water and lasting
79 from a few weeks to a few years at the macroscopic scale, is followed by a
80 long-term creep kinetics that is logarithmic with respect to time. In clay-
81 based materials and soils in general, the application of load causes water to
82 be expelled (which is the so-called consolidation process [Terzaghi 1996]) but,
83 once the excess fluid pressure is dissipated, soils creep logarithmically with
84 respect to time [Lambe & Whitman 1969].

85 The origin of this logarithmic creep in both cementitious and clay-based
86 materials has been much disputed. For cementitious materials, an explana-
87 tion was provided by the so-called microprestress solidification theory [Bažant
88 *et al.* 1997], which recognizes the importance of disjoining pressures and the
89 effect they can have on viscosity. The principle of the theory is the following:
90 The hydration processes in cementitious materials and the restraint induced

91 by the heterogeneous and disordered microstructure prevent an instant-
92 neous release of the high average tensile disjoining pressure prevailing in the
93 C-S-H nano-pores. This disjoining pressure, acting perpendicularly to the C-
94 S-H layers, will be denoted as S and called microprestress (“nanoprestress”
95 though might be a more accurate term, but the “microprestress” is by now
96 well established). The microprestress initially develops as a consequence of
97 clinker hydration. Later it changes with moisture content and temperature
98 and, in absence of mechanical load on concrete, dominates the stresses in
99 solid microstructure [Bažant *et al.* 1997]. The microprestress theory recog-
100 nizes that the apparent viscosity (denoted as η) associated with the sliding
101 of two C-S-H layers over each other is sensitive to this microprestress, i.e.,
102 $\eta = \eta(S)$. The theory then recognizes that, because of the disordered and
103 isotropic nature of C-S-H at the meso-scale, this microprestress in one layer
104 must induce in layers of different orientation shear forces acting parallel to
105 these layers (see Fig. 1). Based on those features, one can show that, for any
106 power-law dependence of the viscosity on the microprestress (i.e., $\eta \propto 1/S^{p-1}$
107 with $p - 1 > 0$), the viscosity evolves linearly with time t , i.e., $\eta \propto t$ (see
108 section for a detailed derivation). For a constant stress, we thus obtain a
109 creep rate that declines in proportion to the inverse of time, and thus a creep
110 strain that increases with time logarithmically.

111 Recognizing the potential role of the enormous tensile stresses induced
112 by disjoining pressures, we aim in the present work at clarifying this role
113 numerically, considering a simplified model system. The system consists

114 of two solid layers that are parallel to each other, with an interlayer pore
115 space between them. The interlayer fluid is modeled as a continuum, and
116 only an effective potential between atoms of the opposite adjacent layers is
117 introduced. Given their high stiffness [Shahsavari *et al.* 2009; Carrier *et al.*
118 2014], the solid layers are considered as rigid.

119 Here we aim at identifying the energy landscape that the system of two
120 layers will be exposed to while sliding over each other. The energy barriers
121 and how they evolve with disjoining pressure effects (i.e., with the micropre-
122 stress) will be translated into the dependence of the apparent viscosity on
123 the microprestress. The relevance of the numerical results with respect to
124 the microprestress theory will be discussed. A comparison with creep data
125 obtained on cementitious materials at various temperatures and relative hu-
126 midities will be performed.

127 **Shearing of infinite plates interacting through** 128 **Lennard-Jones potential**

129 We consider two rigid and infinite plates that are parallel to each other.
130 Each plate consists of atoms located on a square lattice (see Fig. 2). All
131 lengths of the problem are made dimensionless by dividing them by the lattice
132 parameter a : Thus, the dimensionless distance between two closest-neighbor
133 atoms within a plate is equal to unity. The two plates are separated by a
134 distance called the basal spacing: Its value, made dimensionless upon division

135 by the lattice parameter, is denoted as z . The in-plane principal directions
 136 of the two plates are considered aligned at all times and are denoted as \underline{e}_x
 137 and \underline{e}_y ; x and y are the dimensionless relative displacements of the top plate
 138 with respect to the bottom one in the \underline{e}_x and \underline{e}_y directions, respectively. The
 139 origin of the relative displacements is chosen such that the two plates are in
 140 an eclipsed configuration when $x = 0$ and $y = 0$.

141 The i -th atom of one plate interacts with the j -th atom of the other plate
 142 through a Lennard-Jones potential:

$$\Psi(r) = \Psi_0 \left[2 \left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right], \quad (1)$$

143 where r is the dimensionless distance between the two atoms, r_0 is the di-
 144 mensionless equilibrium distance of the Lennard-Jones potential, and Ψ_0 is
 145 the depth of the energy well. This interaction potential should be interpreted
 146 as an effective one, in the sense that it aims at capturing not only the direct
 147 wall-wall interaction, but also the electrostatic and entropic effects due to the
 148 presence of the interlayer water, as well as the water-wall interactions. All the
 149 energies in the system are made dimensionless by dividing them by the depth
 150 of the energy well of this Lennard-Jones potential. Thus, the dimensionless
 151 depth of the energy well of the Lennard-Jones potential is equal to unity.
 152 Note that, by introducing a characteristic energy (i.e., the depth Ψ_0 of the
 153 energy well of the Lennard-Jones potential) and a characteristic length (i.e.,
 154 the lattice parameter a), we define a characteristic force Ψ_0/a , with respect

155 to which all forces introduced in the problem will be made dimensionless.

156 Given the periodicity of the system, all the atoms are equivalent one to
157 the other. Therefore, from now on, we focus on the energy of only one atom
158 of one plate interacting with all the atoms of the other plate. The energy of
159 interaction of this atom is $\sum_i \Psi(r_i)$, where r_i is the dimensionless distance
160 that separates the atom of interest from the atom i in the other plate.

161 We consider that the atom of interest is subjected to a (dimensionless)
162 force F acting parallel to the layers in the \underline{e}_x direction, and to a (dimension-
163 less) tensile force S normal to the layers, i.e., in the \underline{e}_z direction (this force
164 is the microprestress). Under the action of those forces, the energy E of the
165 atom of interest is:

$$E = \sum_i \Psi(r_i) - Sz - Fx. \quad (2)$$

166 For a given microprestress S and transversal load F , the energy landscape
167 to which the system is exposed upon a displacement in the \underline{e}_x direction (i.e.,
168 upon sliding of the two layers over each other) is obtained as follows. At a
169 given relative displacement x , for a fixed relative displacement $y = 0.5$, the
170 energy E is minimized with respect to the distance z between the two plates
171 (indeed, we checked that, at given x , minimizing the energy with respect
172 to y and z yields $y = \pm 0.5$): Thus, at the given relative displacement x ,
173 the equilibrium z -position of the layer is determined, and the energy E of
174 this equilibrium state is stored. This calculation is repeated for a variety

175 of relative displacements x . Note that, in these calculations, the force S
176 normal to the layers is kept constant: When the relative displacement x
177 evolves, the z -position of the layer (i.e., the interlayer spacing) varies. Said
178 otherwise, shear induces volume variations, as noted by Hoang & Galliero
179 (2015). However, the C-S-H layers being surrounded by the solid C-S-H gel,
180 this variation of the z -position would be partly prevented and thus translate
181 into variations of the force S : Here, we neglect this effect.

182 The results for a dimensionless equilibrium distance $r_0 = 1$ are displayed
183 in Fig. 3. Calculations for microprestress $S > 6$ were not possible, because
184 such microprestress suffices to separate the two plates from each other. First,
185 one observes that, in absence of any transversal load or microprestress, equi-
186 librium positions are at $x = \pm 0.5$, i.e., when the two plates are in a stag-
187 gered position with respect to each other. For the plate to be translated from
188 $x = -0.5$ to $x = 0.5$, the system needs to overcome an energy barrier, which
189 we denote as ΔE . In absence of a transversal load F , an increase of the
190 microprestress S decreases this energy barrier. Furthermore, application of a
191 transversal load F imposes on the energy landscape an asymmetric tilt. This
192 induced tilt causes a decrease of the energy barrier that the plate needs to
193 overcome in order to move in the specified direction of the transversal load,
194 and to an increase of the energy barrier that the plate needs to overcome in
195 order to move in the reverse direction. This favors the sliding in the direction
196 of the transversal load.

197 Based on energy landscapes such as the ones displayed in Fig. 3, one

198 can calculate how the energy barrier ΔE required for the plate to move
 199 by one lattice spacing in the direction of the transversal load evolves with
 200 the various loadings. The calculated energy barriers are displayed in Fig. 4.
 201 We may distinguish two regimes, at low and high microprestress. When
 202 the microprestress is low enough, then, for any transversal load, the energy
 203 barrier ΔE decreases linearly with the normal force S , i.e., $\Delta E = c_1 - c_2 S$,
 204 where c_1 and c_2 are functions of the transversal load. In contrast, when
 205 the microprestress S is high enough, then, for any transversal load F , the
 206 energy barrier ΔE decreases linearly with the logarithm of the normal force
 207 S , i.e., $\Delta E = c_3 - c_4 \ln(S)$. Again, the coefficients c_3 and c_4 depend on the
 208 transversal load.

209 In an isotropic solid such as C-S-H on the mesoscopic scale, the micro-
 210 prestress S must induce a transversal load F . Reasonably, one can assume
 211 that this transversal load will represent a fraction of the microprestress S .
 212 For various ratios F/S of the transversal load F to the microprestress S , we
 213 plot how the energy barrier for dimensionless equilibrium distance $r_0 = 1$
 214 depends on the microprestress S ; see Fig. 5a. For large enough micropre-
 215 stresses S , we observe a clear logarithmic dependence of the energy barrier
 216 on the microprestress S , i.e. $\Delta E = \alpha_1 - \alpha_2 \ln(S)$. Interestingly, to first order,
 217 the coefficient α_2 does not depend on the ratio F/S . Therefore, independent
 218 of this ratio (which we do not know, as it is a consequence of the spatial
 219 orientation of the microstructure, of the elastic properties of the phases, and
 220 of the hydration process), the energy barrier ΔE decreases linearly with the

221 logarithm of the stresses.

222 Over this latter range of large enough microprestress, when introducing
223 an Arrhenius-type dependence of viscosity on the energy barrier [Debenedetti
224 & Stillinger 2001; Nabarro 2001], i.e.,

$$\eta \propto \exp(\Delta E/k_B T), \quad (3)$$

225 we find, for the apparent viscosity η associated to the sliding of the two layers
226 over each other, the following relation:

$$\eta \propto \exp\left(\frac{\alpha_1 - \alpha_2 \ln(S)}{k_B T}\right) = \exp\left(\frac{\alpha_1}{k_B T}\right) \left(\frac{1}{S}\right)^{\alpha_2/k_B T}. \quad (4)$$

227 Since $\eta \propto 1/S^{p-1}$ with $p-1 > 0$, we thus observe, for large microprestress, a
228 dependence of viscosity on microprestress that can justify the microprestress
229 theory (see section).

230 In terms of orders of magnitude, we find out that the dimensionless en-
231 ergy barriers ΔE are on the order of unity (see Fig. 4). It follows that the
232 energy barriers are on the order of Ψ_0 and thus, classically for Lennard-Jones
233 potentials, on the order of 10^{-21} J. Those energy barriers are therefore of the
234 same order of magnitude as $k_B T \approx 10^{-21}$ J at $T = 300$ K. Therefore, the
235 proposed mechanism of a viscosity affected by the energy barriers due to the
236 effective wall-wall interaction is plausible. In terms of stresses at stake, the
237 dimensionless normal forces considered in the study are on the order of unity
238 as well (see Fig. 4), i.e., the normal forces are on the order of Ψ_0/a . Those

239 normal forces translate into normal stresses on the order of Ψ_0/a^3 , i.e., into
240 normal forces on the order of $1 \text{ eV} / (1 \text{ nm})^3 \approx 10^8 \text{ Pa} = 100 \text{ MPa}$. There-
241 fore, the characteristic stresses considered in this study are on the order of
242 the stresses induced by disjoining pressures in real systems.

243 The fact that the model nano-scale system we here propose (see Fig. 2)
244 makes it possible to retrieve the micoprestress theory, and hence a long-term
245 creep of cementitious materials that evolves with time as a logarithmic func-
246 tion, may look surprising at first glance. Indeed, C-S-H layers are made of
247 several chemical elements and are complex chemically. Therefore, with re-
248 spect to natural C-S-H, or even to already existing C-S-H molecular models
249 (see, e.g., Taylor (1986); Richardson (2008); Pellenq *et al.* (2009)), our model
250 is crude, in the sense that it fully neglects the chemistry of C-S-H. The fact
251 that, in spite of this crudeness, our system makes it possible to retrieve the
252 micoprestress theory, shows that the logarithmic feature of long-term creep
253 of cementitious materials does not originate from any chemical specificity
254 of C-S-H. Such a conclusion is consistent with the experimental observation
255 that clays also creep logarithmically with respect to time in the long term,
256 although the chemical composition of the clay layers differs from the chem-
257 ical composition of C-S-H. In contrast, the feature that our system keeps
258 in common with C-S-H is that it is a nano-porous layered material. This
259 observation hints towards a logarithmic creep of cementitious materials that
260 would originate from the fact that C-S-H is a nano-porous layered material.

261 **Dependence of viscosity on microprestress, tem-** 262 **perature and water content**

263 The model we have formulated allows us to deduce a dependence of viscosity
264 on microprestress that is consistent with the microprestress theory. We now
265 aim at determining whether this model makes it possible to retrieve the ob-
266 served dependence of creep of cementitious materials on water content and
267 temperature. Since this model makes it also possible to retrieve a creep that
268 evolves logarithmically with respect to time, the comparison with experi-
269 mental data for cementitious materials is restricted to the long-term creep,
270 which does evolve logarithmically with respect to time. To compare our
271 model with the existing data, we first review the main steps of the derivation
272 of the microprestress theory, as presented next.

273 **Dependence on temperature**

274 Let us now focus on the effect of temperature on the viscosity predicted by
275 our model, and on the consistency of this prediction with the phenomenology
276 of long-term creep of cementitious materials. The derivation of the micro-
277 prestress theory proceeds as follows [Bažant *et al.* 1997]:

278 The shear stress, τ , applied to the C-S-H layers may be expressed as
279 $\tau = \eta \dot{\epsilon}$ where η is the viscosity, ϵ is the shear strain, and $\dot{\epsilon}$ is the shear strain
280 rate, which characterizes the sliding of the two parallel layers over each other.
281 The relaxation of the microprestress S is imagined to be the result of a creep

282 (or flow) of similar origin, resisted by a spring of stiffness K_S coupled in
 283 series, as sketched in Fig. 1. Thus, the equation governing the relaxation
 284 process is:

$$\frac{\dot{S}}{K_S} + \frac{S}{\eta(S)} = 0. \quad (5)$$

285 The viscosity must depend on the microprestress S , and since no character-
 286 istic value of this dependence is known, the dependence must be self-similar,
 287 i.e., a power law:

$$\eta = \frac{1}{\alpha} \frac{1}{S^{p-1}} \quad (\text{with } p > 1), \quad (6)$$

288 where p and α are constants. Differential equation (5) may then be solved
 289 and one gets $S^{1-p} = \alpha K_S (p-1)t$. The evolution of the viscosity with time
 290 then follows:

$$\eta = K_S (p-1)t. \quad (7)$$

291 By comparing Eq. (6) with Eq. (4), we find that $p-1 = -\alpha_2/(k_B T)$.

292 At the scale of a macroscopic concrete specimen, a constant uniaxial stress
 293 σ_u is thus expected to cause the axial strain rate $\dot{\epsilon}_u \propto \sigma_u/\eta$. Therefore, the
 294 material compliance $\dot{J}_u = \dot{\epsilon}_u/\sigma_u$ defining the creep is expected to evolve as:

$$\dot{J}_u \propto \frac{1}{\eta} = \frac{k_B T}{K_S \alpha_2} \frac{1}{t}. \quad (8)$$

295 This equation shows that, as anticipated, the power-law dependence (4) of
 296 the viscosity on the microprestress translates into a creep rate that decreases
 297 as $1/t$. Therefore, after integration, one finds that the long-term creep evolves

298 logarithmically with respect to time.

299 From Eq. (8), one may expect that the rate of this long-term logarithmic
300 creep should scale linearly with the temperature T . Said otherwise, the
301 parameter $c_u = t\dot{J}_u$, which is independent of time when the creep is logarithmic,
302 should be proportional to the temperature T . For a few concrete
303 specimens, for which the basic creep (i.e., the creep at no moisture exchange)
304 has been measured at various temperatures (see the data in Nasser & Neville
305 (1965); York *et al.* (1970); Kommendant *et al.* (1976), gathered in Bažant
306 *et al.* (2004)), we display in Fig. 6a the parameter $c_u = t\dot{J}_u$ as obtained by
307 the optimal fitting of creep data in the range within which the creep was ac-
308 tually logarithmic in time. From the experiments, we find that the parameter
309 $c_u = t\dot{J}_u$ is not proportional to the temperature T .

310 A reason for this more complex scaling can be found in the behavior of the
311 interlayer water, the effect of which we have for now discarded. Indeed, for
312 the two C-S-H layers to slide over each other, we need not only to displace the
313 two layers respectively to each other, but we also need to shear the interlayer
314 water. In the numerical study performed in Sec. , the calculated energy
315 barriers are those corresponding only to the relative displacement of the two
316 C-S-H layers. Those energy barriers can be modified by the presence of water
317 (as will be seen in Sec.), as interlayer water screens the interactions between
318 the C-S-H layers, but this screening is only a consequence of the *presence*
319 of the interlayer water, not of its *shearing*, the contribution of which does
320 therefore not appear explicitly in Eq. (8). However, on top of the contribution

321 of the energy barriers, the strain rate at which the C-S-H layers slide on each
 322 other must also depend on the viscosity η_w of the interlayer water. In fact,
 323 the strain rate and the viscosity of the interlayer water should be inversely
 324 proportional to each other. An analogy to justify why it should be so is that of
 325 a horse that runs erratically and encounters fences on his way, over which he
 326 has a given probability of succeeding in jumping; The average speed at which
 327 the horse will move away from his starting point will depend on both his true
 328 speed (which is the analogous of the inverse of the interlayer water viscosity)
 329 and this probability: If the probability for him to succeed in jumping over
 330 the fences does not change, if he runs twice as fast, on average he will reach a
 331 given distance twice as fast. This observation makes it possible to formulate
 332 the unknown proportionality factor in the scaling relation (8), which can be
 333 rewritten as:

$$\dot{J}_u \propto \frac{1}{\eta_w} \frac{k_B T}{K_S \alpha_2} \frac{1}{t}, \quad (9)$$

334 where η_w is the viscosity of the interlayer water. To check the validity of
 335 this modified scaling relation, we use the experimental data displayed in
 336 Fig. 6a to plot the parameter $t\dot{J}_u\eta_w/T$. The viscosity $\eta_w(T)$ of the inter-
 337 layer water is approximated by the viscosity of bulk water: Its values at
 338 various temperatures are obtained from the NIST standard reference data
 339 (<http://webbook.nist.gov/chemistry/fluid/>). Interestingly, one observes in
 340 this figure no specific trend of the parameter $t\dot{J}_u\eta_w/T$ with respect to tem-

341 perature: For a given concrete, this parameter remains roughly constant.

342 The foregoing observation validates a model for the creep of layered C-
343 S-H which in essence consists of two mechanisms: 1) interactions between
344 adjacent C-S-H solid layers, which induce energy barriers that need to be
345 overcome, and 2) viscosity of the interlayer fluid itself, which we model as
346 a continuum with properties identical to those of the bulk fluid. The fact
347 that such a model enables us to capture reasonably well the dependence of
348 long-term creep on temperature can seem surprising, since in this model the
349 interlayer water is considered as bulk water, while the physical properties of
350 confined and bulk water are known to differ significantly from each other:
351 For instance, some find out that, for hydrophilic surfaces, the viscosity of
352 confined or interfacial water differs from the viscosity of bulk water by a
353 factor of about 3 [Raviv *et al.* 2001; Sendner *et al.* 2009]. However, note
354 that the relative dependence of the viscosity of confined and bulk water on
355 temperature might be quite similar, in which case the parameter $t\dot{J}_u\eta_w/T$
356 (see Fig. 6b) would still remain constant with temperature if η_w was the
357 actual viscosity of the confined interlayer water.

358 **Dependence on relative humidity or water content**

359 We now proceed to investigate the effect of relative humidity or water con-
360 tent on the viscosity, as predicted by our model, and the compatibility of
361 this prediction with the phenomenology of long-term creep of cementitious
362 materials. In our model, we will consider that the depth of the energy well

363 does not vary upon when the water content increases, and that the only as-
364 pect that varies is the equilibrium spacing between the two solid plates. In
365 other words, to model an intake of water in the interlayer space, only the
366 equilibrium distance r_0 in the interaction potential (1) is modified, but not
367 the depth Ψ_0 of the energy well.

368 The energy barriers calculated for various equilibrium distances and under
369 various loadings are depicted in Fig. 5. As already observed in section
370 where calculations are performed for an equilibrium distance $r_0 = 1$, the
371 energy barriers for all equilibrium distances considered decrease, at large
372 microprestress, linearly with the logarithm of the microprestress. They do
373 so at a rate that is independent of the ratio F/S . However, this rate of
374 decrease depends on the equilibrium distance, as can be observed in Fig. 7,
375 which shows the coefficient $-dE/d(\ln S) = \alpha_2$ calculated for the range of
376 high microprestress.

377 The goal now is to compare our calculations with the experimental data
378 on how creep at moisture equilibrium varies with the relative humidity. To
379 do so, we use data by Zhang (2014), who performed microindentations on
380 compacted specimens of C-S-H powders equilibrated at various relative hu-
381 midities. Using micromechanics, they back-calculated the creep properties
382 of the C-S-H particles. The creep properties he measured by indentation are
383 condensed into the so-called contact creep modulus C [Vandamme & Ulm
384 2009]. Zhang et al. showed that this creep modulus is inversely proportional
385 to the parameter $c_u = t\dot{J}_u$ [Zhang *et al.* 2014], which is constant during

386 the logarithmic long-term creep of cementitious materials. Their results are
387 presented in Fig. 8a.

388 At the various constant relative humidities considered, the water con-
389 tent is found from the data obtained by Feldman (1973) and reanalyzed by
390 Jennings in the form of adsorption isotherms of C-S-H [Jennings 2008] (see
391 Fig. 8b). To prepare their specimens, Zhang et al. dried the C-S-H powder
392 that they manufactured, rewetted the powder to compact the specimens, and
393 then equilibrated the compacted specimens at the desired relative humidity.
394 Here we consider the second drying isotherm among the isotherms collected
395 by Jennings.

396 In the driest state possible (i.e., when all evaporable water has left C-S-
397 H), the stoichiometric formula for C-S-H is considered to be $C_{1.7}\text{-S-H}_{1.3}$ (in
398 cement chemistry notation). Thus its molar mass is equal to $178.84 \text{ g}\cdot\text{mol}^{-1}$.
399 In this driest state possible, the structure of C-S-H is considered to be close
400 to that of tobermorite 9 \AA , as provided by Bonaccorsi & Merlino (2005)
401 and recalled by Richardson (2008), i.e., orthorombic space group Fd2d with
402 $a = 11.16 \text{ \AA}$, $b = 7.32 \text{ \AA}$, $c = 37.40 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$.

403 To approximate this structure with our simple model, we consider that the
404 characteristic spacing between the closest inhomogeneities within each C-S-H
405 layer is $\sqrt{11.16 * 7.32} = 9.03 \text{ \AA}$, and that the basal spacing is $37.40/4 = 9.35$
406 \AA . In this driest state, the thickness of the interlayer water is considered to be
407 null. At larger water contents, we consider that the interlayer space is filled
408 with bulk water, the molar volume of which is $18.048 \text{ cm}^3\cdot\text{mol}^{-1}$ at 20°C and

409 0.1 MPa (these data are taken from the NIST standard reference available
 410 at <http://webbook.nist.gov/chemistry/fluid/>). By a simple geometric calcu-
 411 lation, we can thus determine how the mass density of C-S-H (or its basal
 412 spacing) should be related to its water content.

413 The result of this calculation is shown in Fig. 8c, along with the states
 414 of Jennings’s CM-II model for C-S-H [Jennings 2008]. The good agreement
 415 observed indicates that the simple way we used to relate the basal spacing
 416 (or density) of C-S-H to its water content provides reasonable results. In
 417 conjunction with the adsorption isotherm shown in Fig. 8b, these results
 418 make it possible to calculate how the basal spacing of C-S-H must have
 419 depended on the relative humidity in the experiments of Zhang et al. Since
 420 we work with dimensionless data, comparison with our model requires that
 421 the basal spacing be made dimensionless by dividing it by the characteristic
 422 length 9.03 \AA calculated above for tobermorite 9 \AA .

423 As shown by Eq. (8), the presence of the energy barriers that limit, during
 424 the logarithmic creep, the sliding of the C-S-H layers over each other causes
 425 that function $c_u = t\dot{J}_u$ should scale as:

$$c_u = t\dot{J}_u \propto \frac{1}{\alpha_2} \propto -\frac{1}{dE/d(\ln S)} \quad (10)$$

426 Again, as written in section , this contribution of the energy barriers must be
 427 augmented by the contribution of the interlayer water. Note that we consider
 428 the viscosity of the interlayer water not to depend on the layer thickness

429 (i.e., the interlayer water to behave like bulk water). Thus, in absence of
 430 any energy barrier induced by the interactions between the adjacent C-S-H
 431 layers, the apparent viscosity η associated with the sliding of the C-S-H layers
 432 over each other must scale linearly with the inverse $1/d_w$ of the thickness d_w
 433 of the interlayer water. Here, as calculated in the previous paragraph, d_w is
 434 equal to the basal spacing from which 9.35 \AA must be subtracted. Therefore,
 435 the foregoing equation must be modified as:

$$t\dot{J}_u \propto -\frac{d_w}{dE/d(\ln S)} \quad (11)$$

436 The experimental data of Zhang, together with the prediction by the
 437 above equation, are displayed in Fig. 8d, in which the two sets of values are
 438 made dimensionless by dividing them by their value at the relative humidity
 439 of 11%. Below the relative humidity of 60%, the model is in very good agree-
 440 ment with the set of experimental data, which is very satisfactory given the
 441 simplicity of the model. As was the case for the dependence on temperature
 442 (see Sec.), such good agreement of the model with experimental data can be
 443 surprising, since the actual viscosity of the confined interlayer water differs
 444 from that of bulk water, as it depends on confinement, i.e., on the water con-
 445 tent. However, the crudeness of this approximation is somewhat comparable
 446 to the crudeness of the assumption that the depth of the energy well does
 447 not vary upon an increase of water content. Indeed, for hydrophilic surfaces,
 448 according to Raviv *et al.* (2001) and Sendner *et al.* (2009), the viscosity of

449 confined or interfacial water does not differ from the viscosity of bulk water
450 by orders of magnitude but by a factor of about 3.

451 Above a relative humidity of 60%, our model overestimates the exper-
452 imental data, and this overestimation increases with the relative humidity.
453 This discrepancy can probably be explained, at least partly, by the fact that
454 the adsorption isotherm used here (see Fig. 8b) takes into account not only
455 the water in the C-S-H interlayers, but also the water adsorbed at the surface
456 of the C-S-H globules [Jennings 2008]: Therefore, the adsorption isotherm
457 considered here overestimates the amount of water contained solely in the
458 C-S-H interlayers. Other candidates to explain the discrepancy are the as-
459 sumptions of the independence of the viscosity of interlayer water and of the
460 depth of the energy well on confinement.

461 In any case, in spite of the discrepancy observed at large relative humidity,
462 our model makes it possible to capture remarkably well how the long-term
463 logarithmic creep of C-S-H depends on relative humidity below 60%. We
464 recall that our model takes into account both the influence of the interactions
465 between adjacent C-S-H layers and of the viscosity of the interlayer fluid
466 (considered as a bulk fluid).

467 **Conclusions**

- 468 1. A model nano-scale system, made of two parallel solid layers separated
469 by interlayer fluid, is a useful representative of the creep-generating mi-

470 microscopic building blocks in clay-based materials and in calcium silicate
471 hydrates (i.e., C-S-H —the main hydration product in regular Portland
472 cement).

473 2. The creep may be modeled by atomic interactions between two solid
474 layers subjected to shearing that causes the energy barriers to be over-
475 come and thus the two layers to slide over each other. The evolution
476 of these energy barriers in presence of disjoining pressures and shear
477 stresses can be studied numerically.

478 3. When the disjoining pressures and shear forces are considered propor-
479 tional to each other, the energy barriers decrease linearly with the log-
480 arithm of the disjoining pressure, and they do so at a rate that is
481 independent of the ratio between disjoining pressures and shear forces
482 (see Fig. 5).

483 4. This behavior is consistent with the microprestress theory, which makes
484 it possible to explain why, in cementitious materials, the long-term
485 creep evolves in time as a logarithmic function. The logarithmic feature
486 of long-term creep of cementitious materials does not originate from a
487 chemical specificity of C-S-H, but could originate from the fact that,
488 at the nanometric scale, C-S-H is a nano-porous layered material.

489 5. The analysis of experimental data on the long-term logarithmic creep
490 of cementitious materials, with a focus on the creep kinetics, shows

491 that the present model system is able to predict the observed effects of
492 temperature (Sec.) and relative humidity (Sec.), provided that one
493 takes into account: 1) the energy barriers that need to be overcome
494 in order for the two solid layers to slide over each other, and 2) the
495 viscosity of the interlayer fluid. In particular, it is possible to fit the
496 test data while considering the interlayer fluid (i.e., water in this study)
497 to behave like a bulk fluid.

498 6. Although this study is focused on the cementitious materials (i.e., con-
499 crete), it can likely be extended to geomaterials such as clays and clay-
500 based materials, in which the basic microscopic building units are also
501 made of solid layers (i.e., phyllosilicates in the case of clay) with in-
502 terlayer fluid. Indeed, clay-based materials are also known to creep
503 logarithmically in the long term [Lambe & Whitman 1969].

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Figure1

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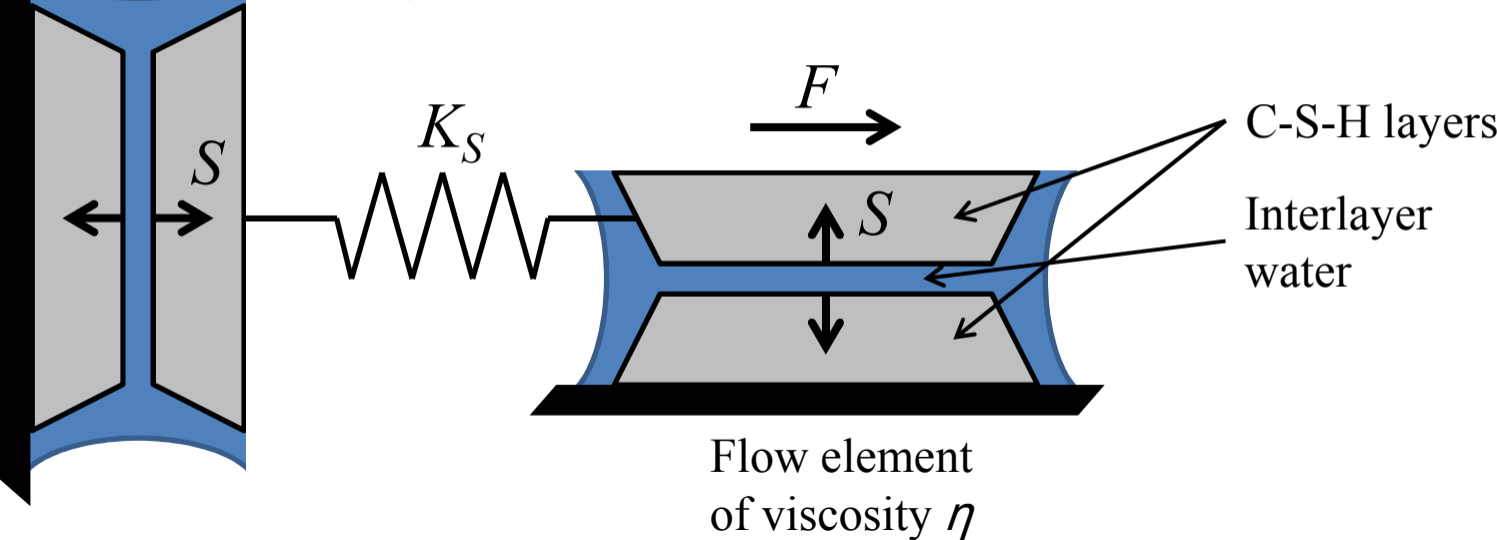
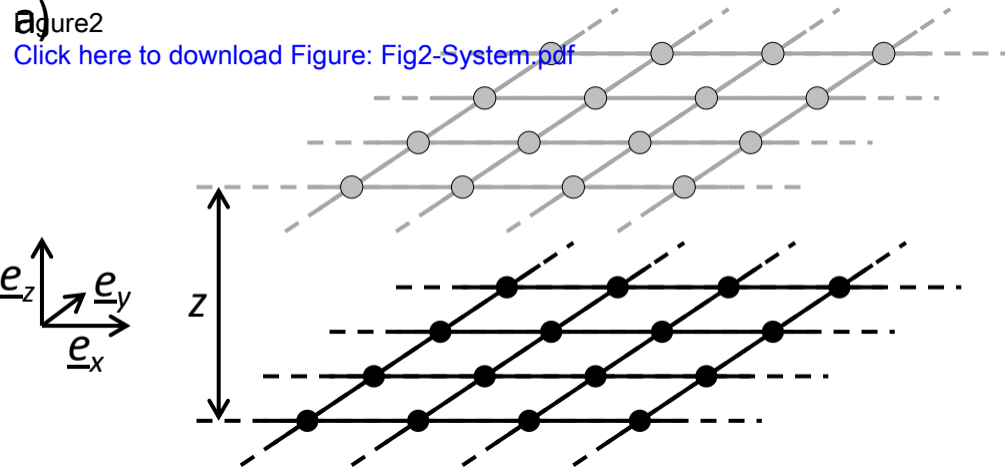


Figure 2

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b)

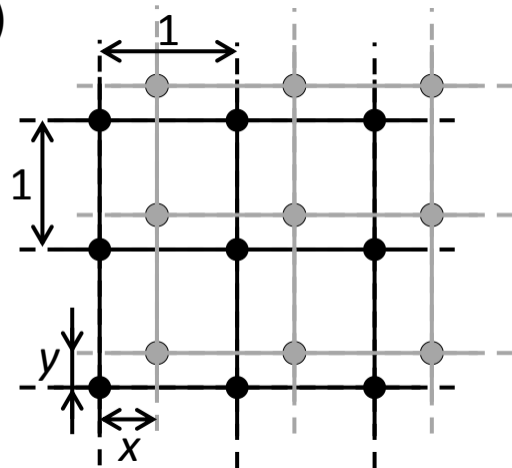
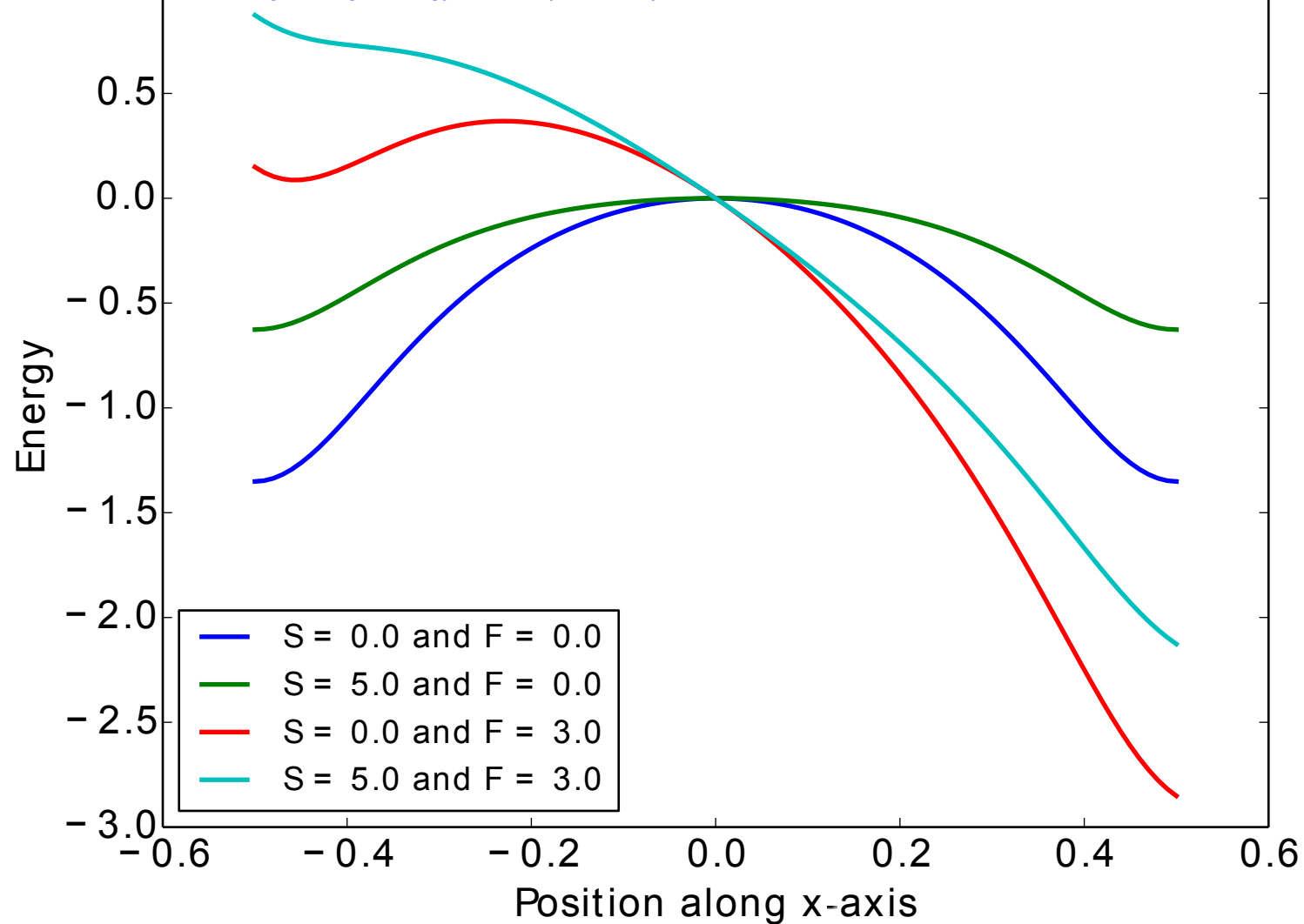


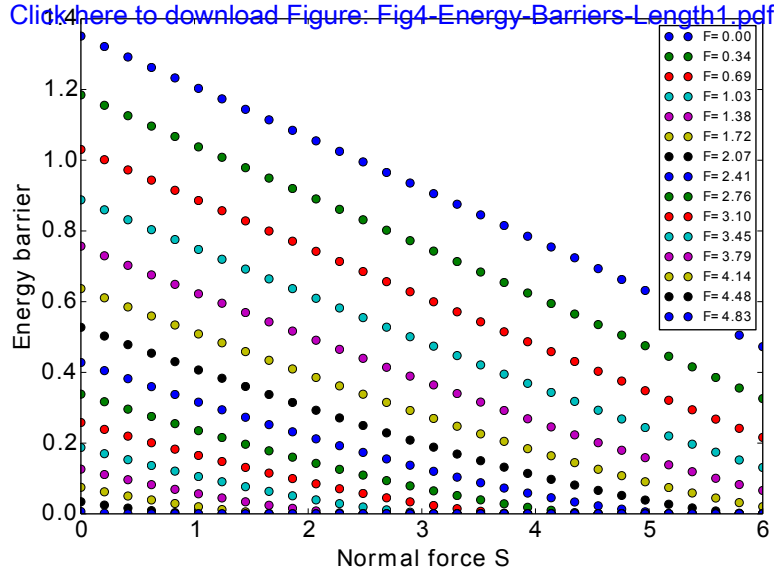
Figure3

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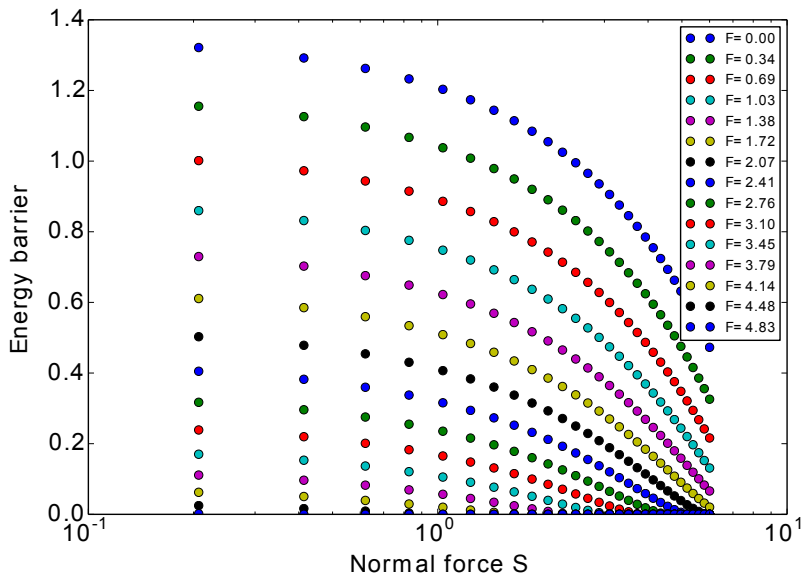


a) figure4

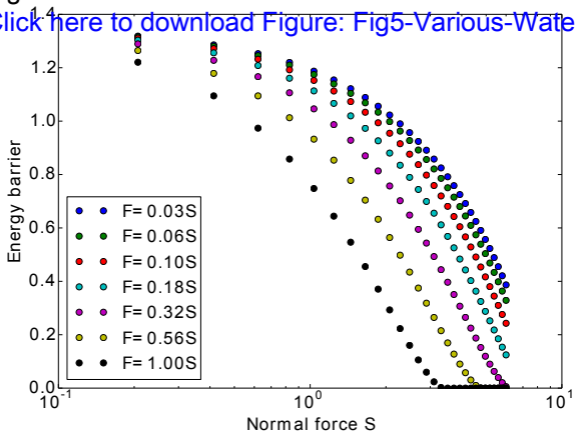
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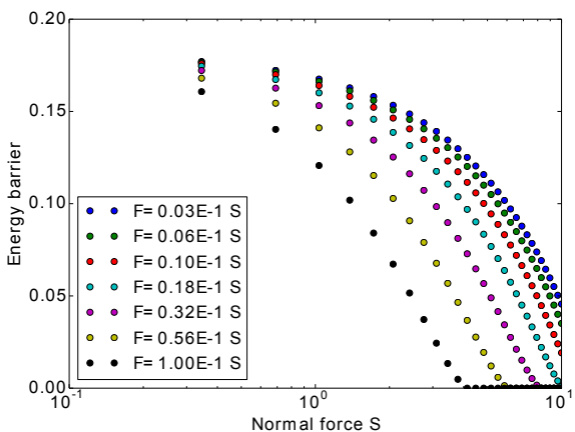
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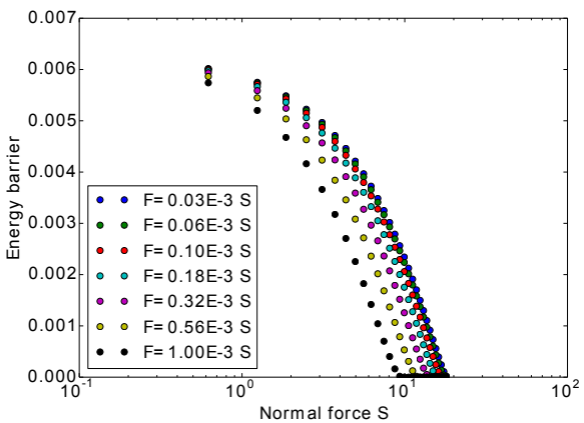
a) figure5

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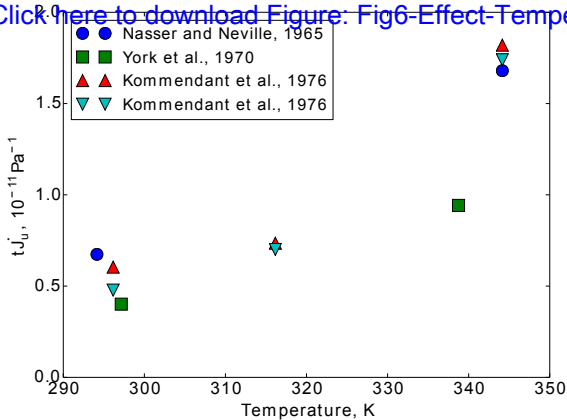
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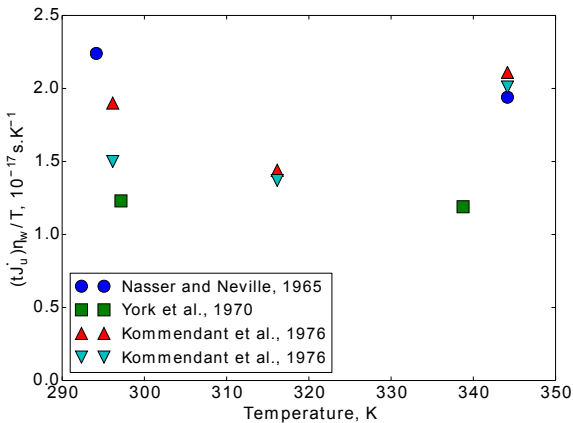
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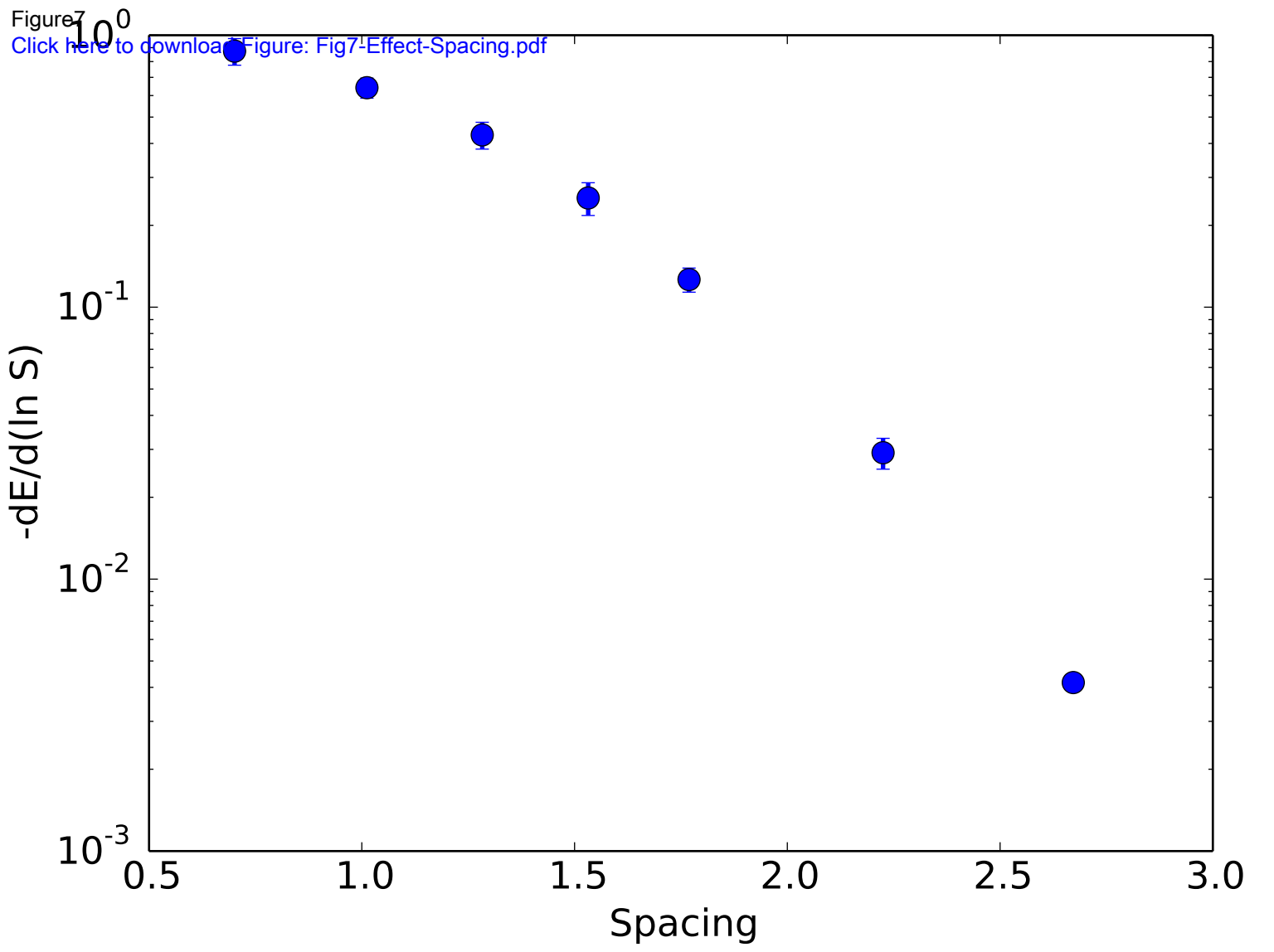


a) figure 6

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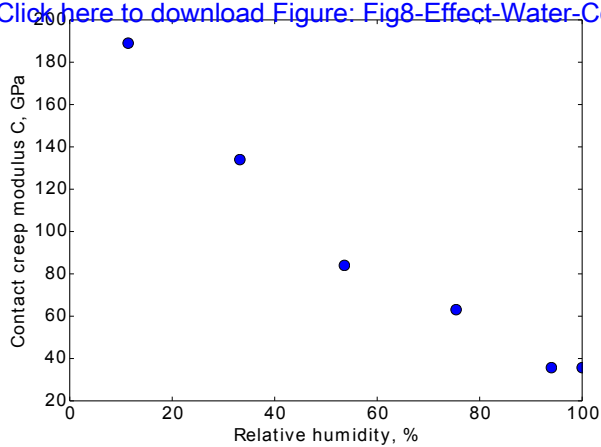
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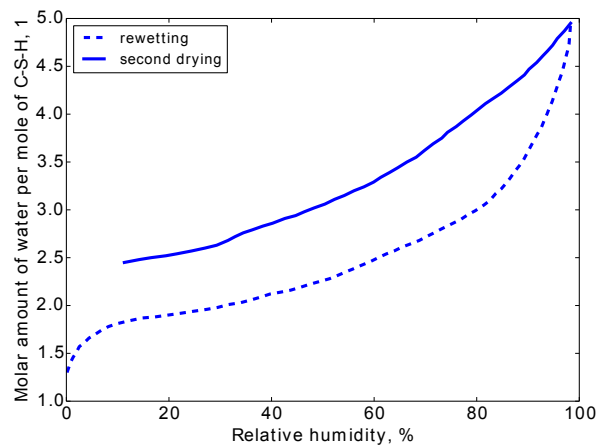


a) Figure 8

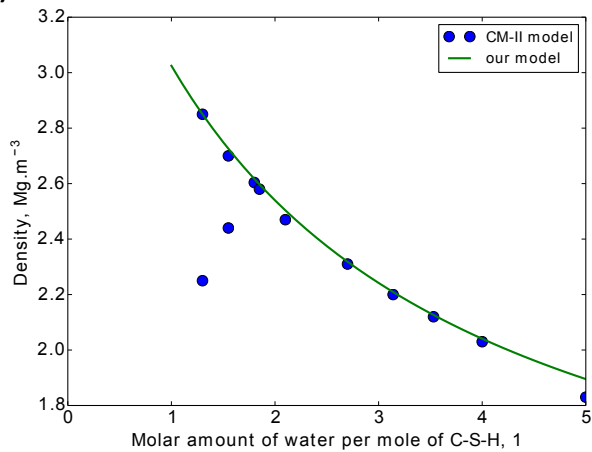
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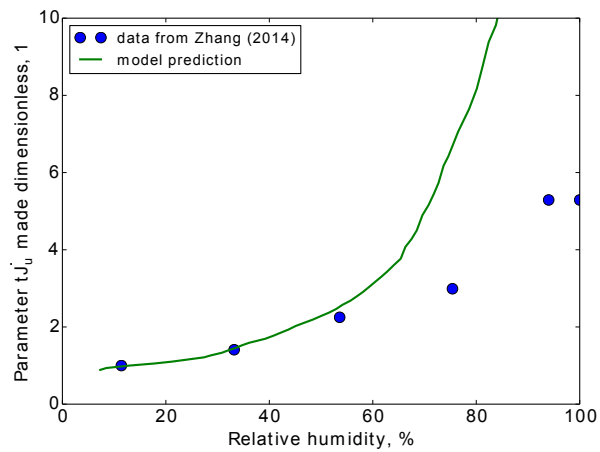
b)



c)



d)



List of figure captions

Figure 1: Principle of the microprestress theory. Adapted from Bažant et al. (1997).

Figure 2: System considered: infinite parallel plates with a square lattice: a) perspective view and b) view in the \underline{e}_z direction. In-between the plates, one finds out the interlayer fluid, modeled as a continuum and not represented on this figure.

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Figure 5: Energy barriers for the transversal motion of infinite rigid plates interacting through Lennard-Jones potential, when the transversal force F is considered to be a fraction of the microprestress σ . Calculations were performed for equilibrium spacing equal to: a) $r_0=1$, b) $r_0=2$, and c) $r_0=3$.

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data on concrete specimens, which can be found in Bažant et al. (2004) and were obtained by Nasser and Neville (1965), York et al. (1970), and Kommendant et al. (1976). The data by Kommendant et al. were obtained by loading the specimens after 28 days of hydration (upward triangles) and after 90 days of hydration (downward triangles).

Figure 7: Effect of basal spacing on how the energy barrier depends linearly on the logarithm of the microstress σ .

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