Creep of lubricated layered nano-porous solids and application to cementitious materials

Matthieu Vandamme, Zdeněk Pavel Bažant, Sinan Keten

► 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-01273134>

Submitted on 10 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

4 Matthieu Vandamme^{*}, Zdeněk P. Bažant^{**}, and Sinan Keten^{***}

5 ^{*}Université Paris-Est, Laboratoire Navier (École des Ponts
6 ParisTech, IFSTTAR, CNRS) 6-8 Av. B. Pascal, 77420
7 Champs-sur-Marne, France

8 ^{**}Department of Civil and Environmental Engineering &
9 Department of Mechanical Engineering & Department of
10 Materials Science and Engineering, Northwestern University,
11 2145 Sheridan Road, Evanston, IL 60208, United States

12 ^{***}Department of Civil and Environmental Engineering &
13 Department of Mechanical Engineering, Northwestern
14 University, 2145 Sheridan Road, Evanston, IL 60208, United
15 States

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; Bazant &
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

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

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

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

where r is the dimensionless distance between the two atoms, r_0 is the dimensionless equilibrium distance of the Lennard-Jones potential, and Ψ_0 is the depth of the energy well. This interaction potential should be interpreted as an effective one, in the sense that it aims at capturing not only the direct wall-wall interaction, but also the electrostatic and entropic effects due to the presence of the interlayer water, as well as the water-wall interactions. All the energies in the system are made dimensionless by dividing them by the depth of the energy well of this Lennard-Jones potential. Thus, the dimensionless depth of the energy well of the Lennard-Jones potential is equal to unity. Note that, by introducing a characteristic energy (i.e., the depth Ψ_0 of the energy well of the Lennard-Jones potential) and a characteristic length (i.e., 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

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

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

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

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

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

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

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

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

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

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

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

This equation shows that, as anticipated, the power-law dependence (4) of the viscosity on the microprestress translates into a creep rate that decreases 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 actually
308 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:

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

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 $178.84 \text{ g.mol}^{-1}$.
399 In this driest state possible, the structure of C-S-H is considered to be close
400 to that of tobermorite $9 \text{ \AA}$, 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 $\text{\AA}$. 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 $18.048 \text{ cm}^3.\text{mol}^{-1}$ at 20°C and

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

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

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

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

Again, as written in section , this contribution of the energy barriers must be augmented by the contribution of the interlayer water. Note that we consider 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 $9.35 \text{ \AA}$ 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

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

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

References

- Bažant, Zdeněk P. 1972. Thermodynamics of interacting continua with surfaces and creep analysis of concrete structures. *Nuclear engineering and design*, **20**, 477–505.
- Bažant, Zdeněk P., & Bazant, Martin Z. 2012. Theory of sorption hysteresis in nanoporous solids: Part I Snap-through instabilities. *Journal of the Mechanics and Physics of Solids*, **60**(9), 1644–1659.

- 511 Bažant, Zdeněk P., Hauggaard, Anders Boe, Baweja, Sandeep, & Ulm, Franz-
 512 Josef. 1997. Microprestress-solidification theory for concrete creep. I: Aging
 513 and drying effects. *Journal of Engineering Mechanics*, **123**(11), 1188–1194.
- 514 Bažant, Zdeněk P., Cusatis, Gianluca, & Cedolin, Luigi. 2004. Temperature
 515 effect on concrete creep modeled by microprestress-solidification theory.
 516 *Journal of engineering mechanics*, **130**(6), 691–699.
- 517 Bažant, Zdeněk P., Hubler, Mija H., & Yu, Qiang. 2011. Pervasiveness of
 518 excessive segmental bridge deflections: Wake-up call for creep. *ACI Struc-*
 519 *tural Journal*, **108**(6), 767–774.
- 520 Bonaccorsi, E., & Merlino, S. 2005. Modular microporous minerals:
 521 cancrinite-davyne group and CSH phases. *Reviews in mineralogy and geo-*
 522 *chemistry*, **57**(1), 241–290.
- 523 Brochard, Laurent, Vandamme, Matthieu, & Pellenq, Roland J.-M. 2012.
 524 Poromechanics of microporous media. *Journal of the Mechanics and*
 525 *Physics of Solids*, **60**(4), 606–622.
- 526 Carrier, Benoit, Vandamme, Matthieu, Pellenq, Roland J.-M., & Van
 527 Damme, Henri. 2014. Elastic properties of swelling clay particles at fi-
 528 nite temperature upon hydration. *The Journal of Physical Chemistry C*,
 529 **118**(17), 8933–8943.
- 530 Debenedetti, Pablo G., & Stillinger, Frank H. 2001. Supercooled liquids and
 531 the glass transition. *Nature*, **410**(6825), 259–67.

532 Espinoza, David N., Vandamme, Matthieu, Pereira, J.-M., Dangla, Patrick,
533 & Vidal-Gilbert, Sandrine. 2014. Measurement and modeling of adsorp-
534 tiveporomechanical properties of bituminous coal cores exposed to CO₂:
535 Adsorption, swelling strains, swelling stresses and impact on fracture per-
536 meability. *International Journal of Coal Geology*, **134-135**(Nov.), 80–95.

537 Feldman, R. F. 1973. Helium flow characteristics of rewetted specimens of
538 dried hydrated Portland cement paste. *Cement and Concrete Research*, **3**,
539 777–790.

540 Hoang, Hai, & Galliero, Guillaume. 2015. Couplings between swelling and
541 shear in saturated slit nanopores: A molecular simulation study. *Physical*
542 *Review E*, **91**(1), 012401.

543 Jennings, Hamlin M. 2008. Refinements to colloid model of C-S-H in cement:
544 CM-II. *Cement and Concrete Research*, **38**(3), 275–289.

545 Kommendant, G. J., Polivka, M., & Pirtz, D. 1976. *Study of concrete proper-*
546 *ties for prestressed concrete reactor vessels, final report-part II, Creep and*
547 *strength characteristics of concrete at elevated temperatures*. Tech. rept.
548 Dept. Civil Engineering, Univ. of California, Berkeley.

549 Lambe, T. W., & Whitman, R. W. 1969. *Soil mechanics*. Wiley.

550 Meunier, Alain. 2005. *Clays*. Springer.

551 Nabarro, F. R. N. 2001. The time constant of logarithmic creep and relax-
552 ation. *Materials Science and Engineering A*, **309-310**, 227–228.

- 553 Nasser, K. W., & Neville, A. M. 1965. Creep of concrete at elevated temper-
 554 atures. *ACI Journal Proceedings*, **62**(12), 1567–1579.
- 555 Pellenq, Roland J.-M., Kushima, Akihiro, Shahsavari, Rouzbeh, Van Vliet,
 556 Krystyn J., Buehler, Markus J., Yip, Sidney, & Ulm, Franz-Josef. 2009. A
 557 realistic molecular model of cement hydrates. *Proceedings of the National*
 558 *Academy of Sciences of the United States of America*, **106**(38), 16102–7.
- 559 Puzrin, Alexander M., Alonso, Eduardo E., & Pinyol, Núria. 2010. Unex-
 560 pected excessive settlements: Kansai international airport, Japan. *Chap.*
 561 *2, pages 23–43 of: Geomechanics of Failures*. Dordrecht: Springer Nether-
 562 lands.
- 563 Raviv, U., Laurat, P., & Klein, J. 2001. Fluidity of water confined to sub-
 564 nanometre films. *Nature*, **413**(6851), 51–54.
- 565 Richardson, Ian G. 1999. The nature of C-S-H in hardened cements. *Cement*
 566 *and Concrete Research*, **29**(8), 1131–1147.
- 567 Richardson, Ian G. 2008. The calcium silicate hydrates. *Cement and Concrete*
 568 *Research*, **38**(2), 137–158.
- 569 Sendner, Christian, Horinek, Dominik, Bocquet, Lyderic, & Netz, Roland R.
 570 2009. Interfacial water at hydrophobic and hydrophilic surfaces: Slip,
 571 viscosity, and diffusion. *Langmuir*, **25**(18), 10768–10781.
- 572 Shahsavari, R., Buehler, Markus J., Pellenq, Roland J.-M., & Ulm, Franz-
 573 Josef. 2009. First-principles study of elastic constants and interlayer inter-

574 actions of complex hydrated oxides: case study of tobermorite and jennite.
575 *Journal of the American Ceramic Society*, **92**(10), 2323–2330.

576 Taylor, H. F. W. 1986. Proposed structure for calcium silicate hydrate gel.
577 *Journal of the American Ceramic Society*, **69**, 464–467.

578 Terzaghi, Karl. 1996. *Soil mechanics in engineering practice*. John Wiley &
579 Sons.

580 Ustinov, E. A., & Do, D. D. 2006. Effect of adsorption deformation on ther-
581 modynamic characteristics of a fluid in slit pores at sub-critical conditions.
582 *Carbon*, **44**(13), 2652–2663.

583 Vandamme, Matthieu, & Ulm, Franz-Josef. 2009. Nanogranular origin of
584 concrete creep. *Proceedings of the National Academy of Sciences of the*
585 *United States of America*, **106**(26), 10552–10557.

586 York, G. P., Kennedy, T. W., & Perry, E. S. 1970. *Experimental investigation*
587 *of creep in concrete subjected to multiaxial compressive stresses and ele-*
588 *vated temperatures*. Tech. rept. Dept. of Civil Engineering, Univ. of Texas,
589 Austin, Tex.

590 Zhang, Qing. 2014. *Creep properties of cementitious materials: effect of*
591 *water and microstructure. An approach by microindentation*. Ph.D. thesis,
592 Université Paris-Est.

593 Zhang, Qing, Le Roy, Robert, Vandamme, Matthieu, & Zuber, Bruno. 2014.

594 Long-term creep properties of cementitious materials: Comparing microin-
595 dentation testing with macroscopic uniaxial compressive testing. *Cement*
596 *and Concrete Research*, **58**, 89–98.

Figure1

[Click here to download Figure: Fig1-PrincipleMicroprestress.pdf](#)

Figure 2

[Click here to download Figure: Fig2-System.pdf](#)

b)

Figure3

[Click here to download Figure: Fig3 Energy Landscape LJ-2D.pdf](#)

a) figure 4

[Click here to download Figure: Fig4-Energy-Barriers-Length1.pdf](#)

b)

a) figure5

[Click here to download Figure: Fig5-Various-Water](#)

b)

c)

a) figure6

[Click here to download Figure: Fig6-Effect-Tempe](#)

b)

a) Figure 8

[Click here to download Figure: Fig8-Effect-Water-Content.pdf](#)

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.

Figure 3: Energy landscape explored by the system upon sliding of the two plates over each other, under the action of a microprestress σ and of a transversal load F .

Figure 4: Energy barriers to the sliding over each other of infinite rigid plates interacting through Lennard-Jones potential, plotted on a) a linear scale and b) a logarithmic scale.

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) $r_0=3$.

Figure 6: Effect of temperature T on a) parameter $\zeta_u = t \cdot \dot{J}_u$ and b) parameter $t \cdot \dot{J}_u \cdot \eta_w / T$. The parameters $\zeta_u = t \cdot \dot{J}_u$ are obtained by fitting experimental creep

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 microprestress σ_s .

Figure 8: Effect of relative humidity on properties of C-S-H. a) Effect of relative humidity on contact creep modulus of C-S-H, measured by microindentation by Zhang (2014). b) Adsorption isotherm of C-S-H upon rewetting and second drying (adapted from Jennings (2008)). c) Effect of water content on basal spacing, according to Jennings's CM-II model (Jennings, 2008), and as predicted by our geometrical calculation. d) Effect of humidity on parameter $\sigma_{cu} = t \cdot \dot{J}_u$ made dimensionless, as back-calculated from the results of Zhang (2014) and as predicted by our model.