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

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Abstract

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

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

³⁸ Introduction

All geomaterials, whether man-made, e.g., cementitious materials in general, or natural, clay-based materials, exhibit creep, i.e., slow deformation over time under the action of sustained mechanical stress. The creep occurs at a rate that can be detrimental to the lifespan of concrete structures and structures on clay foundations [Bažant *et al.* 2011; Puzrin *et al.* 2010]. Cementitious and clay-based materials have in common a phase that confers to ⁴⁵ them most of their viscous properties, is nano-porous and layered.

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

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

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

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

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

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

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

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

Recognizing the potential role of the enormous tensile stresses induced by disjoining pressures, we aim in the present work at clarifying this role numerically, considering a simplified model system. The system consists of two solid layers that are parallel to each other, with an interlayer pore space between them. The interlayer fluid is modeled as a continuum, and only an effective potential between atoms of the opposite adjacent layers is introduced. Given their high stiffness [Shahsavari *et al.* 2009; Carrier *et al.* 2014], the solid layers are considered as rigid.

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

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

We consider two rigid and infinite plates that are parallel to each other. Each plate consists of atoms located on a square lattice (see Fig. 2). All lengths of the problem are made dimensionless by dividing them by the lattice parameter *a*: Thus, the dimensionless distance between two closest-neighbor atoms within a plate is equal to unity. The two plates are separated by a 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:

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

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

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

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

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

$$E = \sum_{i} \Psi(r_i) - Sz - Fx.$$
⁽²⁾

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

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

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

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

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

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

²²¹ logarithm of the stresses.

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

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

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

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

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

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

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 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.

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

Dependence of viscosity on microprestress, tem perature and water content

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

²⁷³ Dependence on temperature

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

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

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

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:

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

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:

$$\eta = K_S(p-1)t. \tag{7}$$

²⁹¹ 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:

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

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

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

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

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

where η_w is the viscosity of the interlayer water. To check the validity of this modified scaling relation, we use the experimental data displayed in Fig. 6a to plot the parameter $t\dot{J}_u\eta_w/T$. The viscosity $\eta_w(T)$ of the interlayer water is approximated by the viscosity of bulk water: Its values at various temperatures are obtained from the NIST standard reference data (http://webbook.nist.gov/chemistry/fluid/). Interestingly, one observes in this figure no specific trend of the parameter $t\dot{J}_u\eta_w/T$ with respect to tem³⁴¹ perature: For a given concrete, this parameter remains roughly constant.

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

³⁵⁸ Dependence on relative humidity or water content

We now proceed to investigate the effect of relative humidity or water content on the viscosity, as predicted by our model, and the compatibility of this prediction with the phenomenology of long-term creep of cementitious materials. In our model, we will consider that the depth of the energy well does not vary upon when the water content increases, and that the only aspect that varies is the equilibrium spacing between the two solid plates. In other words, to model an intake of water in the interlayer space, only the equilibrium distance r_0 in the interaction potential (1) is modified, but not the depth Ψ_0 of the energy well.

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

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

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

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

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

To approximate this structure with our simple model, we consider that the characteristic spacing between the closest inhomogeneities within each C-S-H layer is $\sqrt{11.16 * 7.32} = 9.03$ Å, and that the basal spacing is 37.40/4 = 9.35Å. In this driest state, the thickness of the interlayer water is considered to be null. At larger water contents, we consider that the interlayer space is filled 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 413 of Jenning's CM-II model for C-S-H [Jennings 2008]. The good agreement 414 observed indicates that the simple way we used to relate the basal spacing 415 (or density) of C-S-H to its water content provides reasonable results. In 416 conjunction with the adsorption isotherm shown in Fig. 8b, these results 417 make it possible to calculate how the basal spacing of C-S-H must have 418 depended on the relative humidity in the experiments of Zhang et al. Since 419 we work with dimensionless data, comparison with our model requires that 420 the basal spacing be made dimensionless by dividing it by the characteristic 421 length 9.03 Å calculated above for tobermorite 9 Å. 422

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:

$$c_u = t \dot{J}_u \propto \frac{1}{\alpha_2} \propto -\frac{1}{dE/d(\ln S)}$$
(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 (i.e., the interlayer water to behave like bulk water). Thus, in absence of any energy barrier induced by the interactions between the adjacent C-S-H layers, the apparent viscosity η associated with the sliding of the C-S-H layers over each other must scale linearly with the inverse $1/d_w$ of the thickness d_w of the interlayer water. Here, as calculated in the previous paragraph, d_w is equal to the basal spacing from which 9.35 Å must be subtracted. Therefore, the foregoing equation must be modified as:

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

The experimental data of Zhang, together with the prediction by the 436 above equation, are displayed in Fig. 8d, in which the two sets of values are 437 made dimensionless by dividing them by their value at the relative humidity 438 of 11%. Below the relative humidity of 60%, the model is in very good agree-439 ment with the set of experimental data, which is very satisfactory given the 440 simplicity of the model. As was the case for the dependence on temperature 441 (see Sec.), such good agreement of the model with experimental data can be 442 surprising, since the actual viscosity of the confined interlayer water differs 443 from that of bulk water, as it depends on confinement, i.e., on the water con-444 tent. However, the crudeness of this approximation is somewhat comparable 445 to the crudeness of the assumption that the depth of the energy well does 44F not vary upon an increase of water content. Indeed, for hydrophilic surfaces, 447 according to Raviv et al. (2001) and Sendner et al. (2009), the viscosity of 448

⁴⁴⁹ confined or interfacial water does not differ from the viscosity of bulk water⁴⁵⁰ by orders of magnitude but by a factor of about 3.

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

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

467 Conclusions

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

470 croscopic 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).

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

When the disjoining pressures and shear forces are considered proportional to each other, the energy barriers decrease linearly with the logarithm of the disjoining pressure, and they do so at a rate that is independent of the ratio between disjoining pressures and shear forces (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.
- 5. The analysis of experimental data on the long-term logarithmic creep
 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.

6. Although this study is focused on the cementitious materials (i.e., concrete), it can likely be extended to geomaterials such as clays and claybased 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].

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Normal force S

• • F= 0.00

F= 0.34

F= 0.69

• • F= 1.03

F= 1.38

F= 1.72

• • F= 2.07

• • F= 2.41

F= 2.76

• • F= 3.10

• F= 3.79

0 F= 4.14

• F= 3.45

F= 4.48

F= 4.83

10¹









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 \$S\$ 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 S. 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 $c_u = t \det{J_u}$ and b) parameter $t \det{J_u}$ 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 \$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 Jenning's CM-II model (Jennings, 2008), and as predicted by our geometrical calculation. d) Effect of humidity on parameter $c_u = t \det{J_u}\$ made dimensionless, as back-calculated from the results of Zhang (2014) and as predicted by our model.