



Review History for “The role of disjoining pressure on the drying shrinkage of cementitious materials”

Syeda Rahman, Zachary Grasley

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Summary

The three reviewers raised interesting questions on thermodynamics of porous media and inquired about the relative influence of the disjoining pressure and capillary pressure. The reviewers and the authors also discussed the assumptions that should be made on the microstructure of C-S-H, in particular the pore size distribution.

Review Round 1

Reviewer 1: Ippei MARUYAMA

The manuscript represents the role of disjoining pressure in the simulated cement paste comprehensively. The manuscript contributes much to the field of concrete engineering as well as the related science field. Overall, the manuscript is well-written, and I agree to publish this paper from the journal.

Following are my comments to the authors:

1. L.30, "T" might have been missed.
2. L.44: Capillary condensation under atomic-scale confinement can be considered as a reference (see <https://www.nature.com/articles/s41586-020-2978-1>).
3. L.66 Plassard, C., et al. (2005). "Nanoscale Experimental Investigation of Particle Interactions at the Origin of the Cohesion of Cement." *Langmuir* 21(16): 7263-7270. Plassard, C., et al. (2005). "Nanoscale Experimental Investigation of Particle Interactions at the Origin of the Cohesion of Cement." *Langmuir* 21(16): 7263-7270. can be considered as a reference.
4. L. 172: The reference state is not clear. Which condition becomes zero?
5. L. 187, charge density of what?
6. L. 498, 5nm^2 ? The dimension is not consistent with the "cross-section".
7. Figure 3 and 4, if possible, please show the concentration distribution in the calculated system.

8. Figure 4: The calculation procedure is not clear. 1) How to give the boundary condition? 2) What about the initial state, is this steady-state or unsteady-state calculation?, 3) Regarding Figure 4, less than the certain RH, all the pores should be dried out, in this case, there is no pore solution. How did the author assume this in this calculation? 4) Is the concentration of the solution at the boundary constant? In reality, it could be condensed, so it would be nice to discuss the calculation assumptions. 5) The Liquid saturation degree difference in Figure 4(a) is difficult to consider, please explain. 6) Fig.4(b) shows only the S(RH) ranging from 0.35-1.0, but how to add the S(RH) less than 0.35? Is it just theoretically calculated? If so, the the authors could show the corresponding RH on the X-axis in Fig.4(c).
9. Regarding C-S-H, some researchers say that C-S-H can also change its interlayer space (in part) like in clays. It would be nice to present such a discussion if the authors want to contribute to the problem of C-S-H.
10. In the discussion part, it would be interesting to add the phenomenon of expansion of hardened cement paste under water curing.

Reviewer 2: Abudushalamu AILI

The paper discusses the role of the disjoining pressure on the drying shrinkage of cement based materials. As authors explained well in their introduction, there is significant ambiguity between the roles of the disjoining pressure and of the capillary pressure. Given that the method applied in this paper is original and that the authors support their conclusion with a rigorous derivation, I believe that the publication of the paper would be useful for the community. Nevertheless, I recommend that the authors to revise their manuscript. Here are my comments:

1. In the most important simulation of section 4, figure 4, the authors supposed that two C-S-H particles (or globules) of section 5 nm are situated in a bulk solution. This hypothesis is very different from the real structure of C-S-H, where such globules are closely packed and far from being alone in a bulk solution. I recommend that the authors either modify the simulated unit or discuss more profoundly the advantages and drawbacks of such simplification with regard to the magnitude of the disjoining pressure.
2. I believe that the most important sentence in the paper is at line 536, "Further, one can easily show that the magnitude of shrinkage stress ...". Why is the magnitude of the capillary pressure calculated using the Eq.3 not plotted in Fig.4c so that we can make a better comparison? Another crucial point here is that it seems that the authors compare the magnitude of the shrinkage stress (or disjoining pressure) with that of the capillary pressure. The shrinkage strain is a kind of average strain on the whole volume of the cement paste. When accounting for the contribution of the disjoining pressure and capillary pressure to the shrinkage strain, a weighted-average should be considered as the stress. This is a common approach in poromechanics, see the book of professor Coussy that the authors cited. I would suggest to compare the weighted stress instead of the value of the stress itself to conclude whether the disjoining pressure from osmotic origin is significant or not. The following reference might be useful to get some inspiration on the weighting factor (note that I am not the author of it): El Tabbal, Ginger, et al. "Modelling the drying shrinkage of porous materials by considering both capillary and adsorption effects." *Journal of the Mechanics and Physics of Solids*, 142 (2020): 104016.
3. Still on this modeling of C-S-H, I think tha the authors need to review the literature about pore sizes in C-S-H and check whether the pores always remain fully saturated. With the nuclear magnetic resonance relaxometry (1H-NMR), it is possible to measure the size and volume of gel pores and interlayer spaces which are the two types of porosity in C-S-H. (as an example, Muller, Arnaud CA, et al. "Densification of C-S-H measured by 1H NMR relaxometry." *The Journal of Physical Chemistry C* (2013): 403-412.). In the present study, the authors modeled the disjoining pressure with a pore size of 2 nm, which corresponds the lower side of gel porosity. However, gel pores are known to be dried out with the decrease of relative humidity. So there is an inconsistency between the hypothesis and the reality of C-S-H (at least considered real by many researchers). I think that the authors should modify their basic modeling hypothesis or at least justify their hypothesis with regard to the current knowledge on C-S-H.
4. In the paper, it is assumed that the distance between particles and hence the pore sizes during shrinkage does not change (for instance, see line 433). I agree that the change in pore size of cement paste is small compared to changes observed in clay. This is true only for larger pores but remains arguable for smaller pores, especially with the distance that authors considered in this study. In the reference suggested in the previous paragraph, we see that the interlayer distance and gel pore size decreases (so called densification).

Remarks on details:

- a. There is an inconsistency of sign in Eqs. 1,2 and 3.
- b. Line 59: What do you mean by 'structured water'?
- c. Line 297: 'current approach', do you mean that Coussy's approach in his chapter 2.7.3 is the same as yours, i.e., the conservation of linear momentum?
- d. Line 353: Please give a short explanation to define Debye length.
- e. Line 398: Not all the readers might be familiar with what DLVO theory means.
- f. 4b and c, why is the unit of saturation degree (RH) and not (-)?
- g. Last sentence of the paper: Are you sure that the statement "capillary pressure does not need stable meniscus" is shown in this paper?

Reviewer 3: Yida ZHANG

This manuscript discusses the role of capillary pressure and disjoining pressure in the drying shrinkage of cement paste, with primary focus on the deriving a quantitative model for disjoining pressure. The disjoining pressure model and validated against literature data by solving the model via a finite element analysis. There are several critical issues with the theoretical assumptions and the conclusions of the paper.

1. Introduction: Combining Eq. (1) and (2) will not give Eq. (3). A minus sign is missing somewhere. Also, the first term on the left-hand side of Eq. (1) should be P_{air} rather than P_{vapor} (water vapor is just one small component of air, a gas mixture). The rigorous derivation of Kelvin's Equation (3) involves the integration of Gibbs-Duhem equation of a vapor-liquid system at constant temperature, as give by Coussy (2010) (8.27).
2. Introduction & Conclusion: Rahman and Grasley (2017) seems to be a major reference the current paper is based on. In the conclusion section (line 596-599), the authors explicitly agreed with their point that Eq. (3) is valid with or without menisci. This conclusion is completely unsupported by what is presented in the paper. The theoretical analysis in sections 2-4 is about how disjoining pressure changes with respect to ion concentration and has nothing to do with capillary pressure ($P_{air} - P_{liquid}$). Surely, relative humidity was introduced by the author in Fig. 4 to link with the ion concentration in the pore fluid. This is however a quite indirect link. RH will have direct effect on the shrinkage of porous media even if the pore fluid contain no ions, just due to capillary action along.
3. Following the previous point, it is well accepted that total suction (the right-hand side of Eq. (3)) in a porous media is additively contributed by both metric suction (due to capillarity) plus osmotic suction (due to the presence of ions in the pore water). See Lu and Likos (2004) and many others on this subject. For example, fully saturated clay swells more in pure water than in salt water. In this example, air pressure plays no role, and all the differences are contributed by the osmotic suction alone. How can this effect be captured by Eq. (3) alone for all scenarios with or without menisci? Please elaborate.
4. Eq (5): In thin liquid films, fluid pressure everywhere is highly anisotropic and cannot be described in a spherical tensor. Disjoining pressure works along the direction perpendicular to the film surface. Bulk liquid pressure is preserved along the tangential direction of the film. See de Feijter (1988) and other thin-film physics literatures.
5. The whole theoretical derivation is based on footnote (2): "... assume fluid in the thin film retains bulk fluid property and sufficiently far away from interfaces to neglect surface forces." This is a critical flaw of the paper. Fig. 3b shows that the authors are dealing with disjoining pressure at film thickness of 0-30 nm separation. Many surface forces other than electrostatic force dominant in that range: van der Waals attraction, electrical double layer, hydration force, etc (Israelachvili, 2011). There is no basis to pick just the electrostatic one and neglect all others which can be arguably more dominating (i.e., the hydration force).
6. Even the treatment of the electrostatic force is not rigorous. Ions and counter-ions coexist in an electrolyte solution and the presence of a charged surface will result in the well-established electrical double layer (EDL) repulsion. The authors explicitly assumed in line 267 "... non counterions are adsorbed to the surfaces ... such assumption allows us to neglect the effect of charge regulation". This assumption basically denies EDL, which is non-physical and unfounded.

Some minor comments:

- a. The term “proper” is repeatedly used in the abstract and conclusion sections of the paper. Please define this term.
- b. Lorentz force is mentioned twice in abstract and conclusion. Lorentz force is the combination of electric and magnetic force on a fast-moving point charge due to electromagnetic fields. I don't see how that is relevant to this paper.

References:

- Coussy, O., 2010. Mechanics and physics of porous solids. John Wiley & Sons.
- de Feijter, J.A., 1988. Thermodynamics of thin liquid films, in: Ivanov, I.B. (Ed.), Thin Liquid Films. Marcel Dekker, p. 1.
- Israelachvili, J.N., 2011. Intermolecular and surface forces. Academic press.
- Lu, N., Likos, W.J., 2004. Unsaturated soil mechanics. Wiley.

Authors' Response

We thank you for reviewing our manuscript and giving us the opportunity for resubmitting it. We have made significant modifications to our simulations and manuscript, and we believe that your comments and suggestions have contributed substantially to improving the quality of our manuscript. Please see below our responses to your comments.

Response to Reviewer 1: Ipppei MARUYAMA

1. L.30, "T" might have been missed.

Thank you for noting it. We have revised line 30 to include missing parameters.

2. L.44: Capillary condensation under atomic-scale confinement can be considered as a reference (see <https://www.nature.com/articles/s41586-020-2978-1>).

Thank you for your suggestion. We have added this reference in line 45 of the revised manuscript.

3. L.66 Plassard, C., et al. (2005). "Nanoscale Experimental Investigation of Particle Interactions at the Origin of the Cohesion of Cement." Langmuir 21(16): 7263-7270. Plassard, C., et al. (2005). "Nanoscale Experimental Investigation of Particle Interactions at the Origin of the Cohesion of Cement." Langmuir 21(16): 7263-7270. can be considered as a reference.

Thank you again for your suggestion. We have added this reference in line 71.

4. L. 172: The reference state is not clear. Which condition becomes zero?

The reference state is defined as the initial state with 100% relative humidity. It is customary to define shrinkage stress as the difference between the stress at the reference state to that at any point with lower relative humidity. At 100% relative humidity, the shrinkage stress is zero. We have discussed this point in lines 604-612.

5. L. 187, charge density of what?

Charge density of the charged particles. We modified line 229 to clarify this.

6. L. 498, 5 nm^2 ? The dimension is not consistent with the "cross-section".

Thank you for the correction. We have changed the geometry of our simulation and the text to address other reviewers' comments. Please see the modified texts in line 577 that reads:

“For simulating the effect of disjoining pressure in drying shrinkage of cementitious materials, we consider two square C-S-H particles with a cross-section of 5 nm C-S-H aggregates with a stack thickness of 5 nm and width of 30 nm , as shown in Figure 4a, separated by 210 nm in a continuum characterized by a relative permittivity of 78.5 .”

7. Figure 3 and 4, if possible, please show the concentration distribution in the calculated system.

The concentration distribution between the two charged surfaces can be obtained from the Nernst equation by substituting the electric potential obtained from solving the Poisson-Boltzmann Equation. We did not calculate the distribution directly in our problem. According to the Boltzmann distribution, the ion concentration decreases exponentially from a maximum value from next to the charged surface to a smaller value at the middle of the separation distance. We could show this distribution overlaid onto the mesh, however, the change in concentration for the separation distances considered in the manuscript is so drastic that it would be difficult to discern values from such a plot.

8. Figure 4: The calculation procedure is not clear. 1) How to give the boundary condition? 2) What about the initial state, is this steady-state or unsteady-state calculation? 3) Regarding Figure 4, less than the certain RH, all the pores should be dried out, in this case, there is no pore solution. How did the author assume this in this calculation? 4) Is the concentration of the solution at the boundary constant? In reality, it could be condensed, so it would be nice to discuss the calculation assumptions. 5) The Liquid saturation degree difference in Figure 4(a) is difficult to consider, please explain. 6) Fig.4(b) shows only the S(RH) ranging from 0.35-1.0, but how to add the S(RH) less than 0.35? Is it just theoretically calculated? If so, the the authors could show the corresponding RH on the X-axis in Fig.4(c).

1) Boundary conditions are ascribed to the plate boundaries shown in Fig.4(a), a uniform surface charge density of 0.8 C/m² is assigned to the C-S-H aggregate surfaces (please see line 602), and a zero electric potential is applied to the outer boundaries owing to the overall charge neutrality (please see line 386).

2) An initial concentration of the bulk solution is assumed to be 0.002 M for a relative humidity of 100% (please see line 605). We then calculate the disjoining pressure for a series of discrete concentrations, with each calculation performed at steady state. A sentence has been added to the manuscript to clarify this issue (see line 619). A non-steady state calculation could be done if one wanted to bring transport kinetics into the discussion, but this was beyond the scope of the current work.

"The disjoining pressure is calculated for a series of discrete concentrations, with each calculation performed at steady state."

3) In our computations, we are simulating the reductions in disjoining pressure as ion concentration in the bulk liquid increases. This increase in ion concentration could occur from drying or other sources (e.g., exposure to high ion concentration solution). When due to drying, the reviewer is correct that our model geometry - which assumes a bulk solution surrounding the two surfaces in close proximity to each other - breaks down at low saturation levels. This means that the predicted disjoining pressures at low degrees of saturation are less reliable when the ionic concentration is induced by drying. However, the general trend of decreasing disjoining pressure (increasing shrinkage stress) should yet hold. We have added a clarifying statement to the manuscript (see line 663) to acknowledge the effects of low saturation on our presumed model conditions.

"It is necessary to recognize that the geometry in Figure 4a, which assumes a bulk solution surrounding the two surfaces in close proximity to each other, breaks down at low saturation levels. This means that the predicted disjoining pressures at low degrees of saturation are less reliable when the ionic concentration is induced by drying. However, the general trend of decreasing disjoining pressure (increasing shrinkage stress) should yet hold."

4) The concentration of the solution at the boundary is not constant and can be determined from the Nernst equation by substituting the electric potential obtained from solving the Poisson-Boltzmann equation.

5) We are not sure what you mean by the liquid saturation degree difference in Figure 4(a).

6) The liquid saturation values for relative humidity lower than about 25% were calculated by hypothetically extending the saturation-relative humidity curve to 0% RH. We have shown the hypothetical extension in Figure 4(b). We did not include the humidity on Figure 4(c) because the pressure is really a function of saturation, and not relative humidity. This also justifies the choice of x-axis for Figure 4(c). We have added the following text after line 615 to clarify this.

"Saturation values corresponding to relative humidity lower than 25% have been obtained by hypothetically extending the S-RH curve to 0, as shown by the solid line in Figure 4(b)."

9. Regarding C-S-H, some researchers say that C-S-H can also change its interlayer space (in part) like in clays. It would be nice to present such a discussion if the authors want to contribute to the problem of C-S-H.

C-S-H particles change interlayer spaces and densify during hydration. The densification of C-S-H reaches a plateau and is believed to remain relatively constant after 1-2 days of hydration. We have added this discussion about C-S-H interlayer spacing in lines 534-558. We consider a matured cement paste where hydration is complete and the C-S-H interlayer spacing does not change. We have modified line 596 to clarify this point.

The text at lines 534-558 now reads:

“Muller et al. [2013] have used 1H relaxation nuclear magnetic resonance (NMR) measurements to picture C-S-H morphology as a function of hydration degree for a range of water to cement ratios of cement paste. The experiments show that as the hydration progresses C-S-H grows as a loose-packed assembly of nanocrystalline regions. In these regions the calcium silicate layers are stacked with interlayer water and are interspersed with gel pores with a characteristic size of 3-5 nm that remain relatively constant [Muller et al., 2013]. The NMR data show that the gel porosity and the gel pore size reach a plateau after 1-2 days of hydration, whereas the volume of hydrates continuously grows. The interhydrate pores containing the free water stabilizes at around 8-10 nm, and these pores are not intrinsic to the C-S-H hydrates. The interhydrate pores are comparable in size to the large globule pores suggested by Jennings [2008]. The solid C-S-H density without the gel pores decreases very slightly with the degree of hydration. The bulk C-S-H density that includes the gel water, on the other hand, increases markedly during hydration from around 1.8 g/cm³ at 1 day to 2.65 g/cm³ at 1 year. Muller et al. [2013] suggested that the C-S-H aggregates of layers are approximately 4.2 nm thick, which is close to the globule size suggested by [Jennings, 2008].”

The modified text at line 596 now reads:

“We presume the paste is fully matured so that the C-S-H densification plateaus and there is no notable change in the pore spacing due to the drying process, rather the pore space is gradually invaded by the air filled with vapor.”

10. In the discussion part, it would be interesting to add the phenomenon of expansion of hardened cement paste under water curing.

Thank you for your suggestion. Since water curing of hardened cement paste is essentially a reversed situation to the simulation considered in section 4, we have not simulated this phenomenon separately, rather we have added the following discussion in lines 641-657.

“Similarly, one can simulate the effect of water curing on hardened cement paste by considering the unsaturated or partially saturated cement paste as the starting point and slowly increasing the liquid saturation thereafter. If one immerses a partially saturated hydrated cement paste such that the liquid saturation of the specimen is about 0.4 for instance, into pure water, the water gradually invades the empty dried pores. As the water penetrates the pore network and water saturation increases to 1 (in this case the x-axis in Figure 4(c) is reversed), the water dilutes the salt in big pores, ultimately increasing the difference between the salt concentration in the bulk liquid (in big pores) and in the gap between the charged particles. The increased gradient in electric potential perpendicular to the direction of interparticle gap increases the disjoining pressure, and as a result the hydrated cement paste expands when cured in pure water.”

Response to Reviewer 2: Abudushalamu AILI

1. In the most important simulation of section 4, figure 4, the authors supposed that two C-S-H particles (or globules) of section 5 nm are situated in a bulk solution. This hypothesis is very different from the real structure of C-S-H, where such globules are closely packed and far from being alone in a bulk solution. I recommend that the authors either modify the simulated unit or discuss more profoundly the advantages and drawbacks of such simplification with regard to the magnitude of the disjoining pressure.

We understand that our model is a simplistic view of C-S-H hydrates. While the model does not capture the individual C-S-H particles and/or globules packed closely in an aggregated form, it represents the C-S-H aggregates as a modeling unit and the modeled results should still hold so long as the C-S-H aggregates are separated by thin water layer. It is possible to model multiple closely packed C-S-H particles with different pore sizes representing interlayer and gel pores within the framework of the finite element analysis, simulation of which would be rather computationally expensive. To closely mimic the actual C-S-H structure we have modified our geometry so that the C-S-H aggregates/stacks that are sheet like and are separated by 10 nm (to mimic large globule pores (Jennings 2008) or interhydrate pores (Muller, 2013)). We have also adopted the term “C-S-H aggregates” in lieu of “C-S-H particles” to avoid confusion to readers. The following text has been added in lines 582-596.

“The model adopted here is a simplistic view of C-S-H aggregates and does not represent individual C-S-H particles packed with interlayer and gel water. Simulation of complex C-S-H structures where C-S-H particles are closely packed and are separated by interlayer water and gel water, is still possible under the framework of finite element analysis but is computationally rather expensive. Moreover, if a range of pore sizes from 1 to 10 nm are to be simulated representing interlayer water, gel water, and interhydrate pores, short range surface forces which have been excluded from our simulation, can no longer be excluded. With the simplistic geometry, the modeled results provide the general trend and extend Derjaguin's concept of disjoining pressure to the context of drying shrinkage of cementitious materials.”

2. I believe that the most important sentence in the paper is at line 536, “Further, one can easily show that the magnitude

of shrinkage stress ...". Why is the magnitude of the capillary pressure calculated using the Eq.3 not plotted in Fig.4c so that we can make a better comparison? Another crucial point here is that it seems that the authors compare the magnitude of the shrinkage stress (or disjoining pressure) with that of the capillary pressure. The shrinkage strain is a kind of average strain on the whole volume of the cement paste. When accounting for the contribution of the disjoining pressure and capillary pressure to the shrinkage strain, a weighted-average should be considered as the stress. This is a common approach in poromechanics, see the book of professor Coussy that the authors cited. I would suggest to compare the weighted stress instead of the value of the stress itself to conclude whether the disjoining pressure from osmotic origin is significant or not. The following reference might be useful to get some inspiration on the weighting factor (note that I am not the author of it): El Tabbal, Ginger, et al. "Modelling the drying shrinkage of porous materials by considering both capillary and adsorption effects." *Journal of the Mechanics and Physics of Solids*, 142 (2020): 104016.

The capillary pressure determined by equation (3) is an order of magnitude higher than the magnitude of disjoining pressure, and as a result, when plotted using the same scale, the change in disjoining pressure with respect to relative humidity appears to be very small compared to that in capillary pressure. It will be difficult to discern the disjoining pressure values from such a plot. A plot of the weighted average of these two stresses may serve as a better means to compare the relative contribution and make a great topic for future studies. Such analyses are beyond the scope of this paper. We added the following text below line 663, which discusses the relative contributions of the two mechanisms: "The relative contribution of these two mechanisms can be quantitatively assessed by considering the weighted average of the capillary pressure and disjoining pressure as outlined by El Tabbal et al. [2020] within the framework of poromechanics [Coussy, 2010c]."

3. Still on this modeling of C-S-H, I think that the authors need to review the literature about pore sizes in C-S-H and check whether the pores always remain fully saturated. With the nuclear magnetic resonance relaxometry (1H-NMR), it is possible to measure the size and volume of gel pores and interlayer spaces which are the two types of porosity in C-S-H. (as an example, Muller, Arnaud CA, et al. "Densification of C-S-H measured by 1H NMR relaxometry." *The Journal of Physical Chemistry C* (2013): 403-412.). In the present study, the authors modeled the disjoining pressure with a pore size of 2 nm, which corresponds to the lower side of gel porosity. However, gel pores are known to be dried out with the decrease of relative humidity. So there is an inconsistency between the hypothesis and the reality of C-S-H (at least considered real by many researchers). I think that the authors should modify their basic modeling hypothesis or at least justify their hypothesis with regard to the current knowledge on C-S-H.

We believe that our assumptions on pore sizes in C-S-H are compliant with the experimental findings in the literature. We consider a matured paste which is initially saturated and subject to 100% relative humidity and is subsequently exposed to drying. We show that as the relative humidity decreases, the gel pores dry out, as presented by the reduced liquid saturation (X axis in Figure 4c), and the pore liquid leaves the pore space increasing the solute concentration in the pore solution, the disjoining pressure increases. While as you mentioned that we originally modeled the lower end of the gel pores- equivalent to what Muller (2013) referred to as gel pores and Jennings (2008) referred to as small globule pores- we have revised our geometry to instead capture the interhydrate or large globule pores of about 10 nm. This also justifies the omission of other short range surface forces from our analysis, about which another reviewer raised concerns. We have added the following discussion to provide a brief background on the C-S-H structure, pore characteristics, and densification in lines 534-558.

"Muller et al. [2013] have used 1H relaxation nuclear magnetic resonance (NMR) measurements to picture C-S-H morphology as a function of hydration degree for a range of water to cement ratios of cement paste. The experiments show that as the hydration progresses C-S-H grows as a loose-packed assembly of nanocrystalline regions. In these regions the calcium silicate layers are stacked with interlayer water (≈ 1 nm in size) and are interspersed with gel pores with a characteristic size of 3-5 nm that remain relatively constant [Muller et al., 2013]. The NMR data show that the gel porosity and the gel pore size reach a plateau after 1-2 days of hydration, whereas the volume of hydrates continuously grows. The interhydrate pores containing the free water stabilizes at around 8-10 nm, and these pores are not intrinsic to the C-S-H hydrates. The interhydrate pores are comparable in size to the large globule pores suggested by Jennings [2008]. The solid C-S-H density without the gel pores decreases very slightly with the degree of hydration. The bulk C-S-H density that includes the gel water, on the other hand, increases markedly during hydration from around 1.8 g/cm³ at 1 day to 2.65 g/cm³ at 1 year. Muller et al. [2013] suggested that the C-S-H aggregates of layers are approximately 4.2 nm thick, which is close to the globule size suggested by [Jennings, 2008]."

4. In the paper, it is assumed that the distance between particles and hence the pore sizes during shrinkage does not change (for instance, see line 433). I agree that the change in pore size of cement paste is small compared to changes observed in clay. This is true only for larger pores but remains arguable for smaller pores, especially with the distance that authors considered in this study. In the reference suggested in the previous paragraph, we see that the interlayer distance and gel pore size decreases (so called densification).

You are correct that the C-S-H densification occurs and affect the pore size. However, since we consider matured cement paste whereby hydration is near complete, and the relative densification of the C-S-H can be neglected, the decrease in interlayer space and gel pore size due to hydration should not affect the assumptions associated with the concept presented here,. Furthermore, as mentioned in our previous response, we have modified the separation distance in our simulation from 2 nm to 10 nm in response to an issue raised by another reviewer. We believe that even as the C-S-H densification occurs, pores of this range do not change their size. We have also used the term “hydrated/matured cement paste” throughout the manuscript to clarify this point. We have modified line 596 as follows:

“We also presume *the paste is fully matured so that the C-S-H densification plateaus and there is no notable change in the pore spacing due to the drying process, rather the pore space is gradually invaded by the air filled with vapor.*”

- a. There is an inconsistency of sign in Eqs. 1,2 and 3.

Thank you for pointing out the inconsistency. Equation (2) has been missing a negative sign, and we have fixed it.

- b. Line 59: What do you mean by ‘structured water’?

Structured water is the adsorbed water films that cover C-S-H surfaces. We have added this definition to line 61 as follows:

“They argue that during desiccation structured water (*adsorbed water films that cover cement hydrate surfaces*) evaporates, disjoining pressure decreases, due to attractive forces surfaces come closer, and shrinkage occurs.”

- c. Line 297: ‘current approach’, do you mean that Coussy’s approach in his chapter 2.7.3 is the same as yours, i.e., the conservation of linear momentum?^[2mm] We mean that the disjoining pressure derived in our manuscript yields the same final form derived by Coussy in his chapter 2.7.3. Coussy did not use conservation of linear momentum. We have modified line 306 to clarify this:

“For two plates – with constant surface charge densities – separated by a thin liquid layer containing monovalent ions and counterions, disjoining pressure deduced here using ~~the current approach~~ *the conservation of linear momentum* takes yields the same form derived in ~~{Coussy2010a}~~ *by Coussy [2010a]* for the excess of internal pressure to explain the swelling of clay particles in fresh or salty water.”

- d. Line 353: Please give a short explanation to define Debye length.

The definition of Debye length is not very straightforward, and several interpretations exist in the literature. Chapter 14 - electrostatic forces between surfaces in liquids in Intermolecular and Surface Forces, pages 291–340 in Israelachvili, J. N. (2011) provides extensive discussion of Debye length. We have modified line 404 to include this reference in the manuscript:

“However, approximate solutions are generally only sufficiently accurate for surface separations beyond about one Debye length (*please see [Israelachvili, 2011] for the definition and interpretation of Debye length*) . . .”

- e. Line 398: Not all the readers might be familiar with what DLVO theory means.

We omitted DLVO theory from our text and changed the text at line 450 of the revised manuscript to read “*It does not include the attractive van der Waals forces or other short range surface forces.*”

- f. 4b and c, why is the unit of saturation degree (RH) and not (-)?

S(RH) implies that saturation is a function of RH. We have modified the x-axis to remove the term RH from parentheses to avoid confusion to readers.

- g. Last sentence of the paper: Are you sure that the statement “capillary pressure does not need stable meniscus” is shown in this paper?

While we definitely feel that this is an important statement for the cement community, we agree that you are right, and we did not directly investigate this in the manuscript. We have removed this statement from the conclusion section.

Response to Reviewer 3: Yida ZHANG

1. Introduction: Combining Eq. (1) and (2) will not give Eq. (3). A minus sign is missing somewhere. Also, the first term on the left-hand side of Eq. (1) should be P_{air} rather than P_{vapor} (water vapor is just one small component of air, a gas mixture). The rigorous derivation of Kelvin’s Equation (3) involves the integration of Gibbs-Duhem equation of a vapor-liquid system at constant temperature, as give by Coussy (2010) (8.27).

Thank you for noting the discrepancies in equations (2) and (3). Equation (2) has been missing a minus sign, and we have added it. Equation (1) considers a vapor-liquid system and relates the vapor pressure to the vapor-liquid surface tension. The notation in equation (1) is consistent with the derivation provided by Coussy (2010) (8.27) from the Gibbs-Duhem equation of a liquid-vapor interface. We realize that confusion may arise from different notations (pl vs pl-w) used in equation (1) and (2), and hence we have modified equation (2) and (3) to be consistent with (1).

2. **Introduction & Conclusion:** Rahman and Grasley (2017) seems to be a major reference the current paper is based on. In the conclusion section (line 596-599), the authors explicitly agreed with their point that Eq. (3) is valid with or without menisci. This conclusion is completely unsupported by what is presented in the paper. The theoretical analysis in sections 2-4 is about how disjoining pressure changes with respect to ion concentration and has nothing to do with capillary pressure ($P_{air} - P_{liquid}$). Surely, relative humidity was introduced by the author in Fig. 4 to link with the ion concentration in the pore fluid. This is however a quite indirect link. RH will have direct effect on the shrinkage of porous media even if the pore fluid contain no ions, just due to capillary action along.

The idea of capillary pressure has been presented in the manuscript to show that the capillary pressure and disjoining pressure additively contribute to the drying shrinkage at all relative humidity range. Since the magnitude of the capillary pressure is much higher than the disjoining pressure, we conclude that the capillary pressure is the dominant factor at all relative humidity range and feel that it is important to include this discussion in the manuscript for clarity. We also agree with you that we did not directly investigate the effect of meniscus on capillary pressure. We have removed lines 755-760 from the conclusion section but kept it in the introduction for the completeness of the manuscript.

3. Following the previous point, it is well accepted that total suction (the right-hand side of Eq. (3)) in a porous media is additively contributed by both metric suction (due to capillarity) plus osmotic suction (due to the presence of ions in the pore water). See Lu and Likos (2004) and many others on this subject. For example, fully saturated clay swells more in pure water than in salt water. In this example, air pressure plays no role, and all the differences are contributed by the osmotic suction alone. How can this effect be captured by Eq. (3) alone for all scenarios with or without menisci? Please elaborate.

You are correct, equation (3) alone cannot explain why saturated clay swells more in pure water than in salt water. This is why, we are refraining from defining equation (3) as total suction, as this equation is intended for the liquid-vapor interface of pure water. As mentioned in line 37, this equation can be modified to account for both matric suction and osmotic suction for solutions containing dissolved ions. A modified equation (an equivalent form is presented in equation (4) whose right hand side has two terms-disjoining pressure, which can be osmotic in nature, and capillary pressure) containing both the matric suction and osmotic suction terms implies that the effect of capillary pressure and disjoining pressure are additive in nature and further justifies inclusion of our discussion regarding the capillary pressure in the manuscript.

4. **Eq (5):** In thin liquid films, fluid pressure everywhere is highly anisotropic and cannot be described in a spherical tensor. Disjoining pressure works along the direction perpendicular to the film surface. Bulk liquid pressure is preserved along the tangential direction of the film. See de Feijter (1988) and other thin-film physics literatures.

We agree with you that the total stress is anisotropic. Equations 20-23 of Feijter (1988) state that the total stress tensor is anisotropic. The total stress tensor is the sum of the Cauchy stress and the Maxwell stress. We have separated Maxwell stress from the Cauchy stress and expressed the former in terms of the force vector, f_e . In our case Cauchy stress is spherical but Maxwell stress is not. If we combine these two components, the total stress tensor will be anisotropic and in agreement with Feijter and other thin-film physics literature. We specifically and purposefully decomposed the total stress tensor to avoid precisely the confusion about mechanical stress sphericity induced by using the total stress tensor. That is, our approach clearly demonstrates that electrostatic effects – much like gravitational effects – do not induce shear stresses in Newtonian liquids like water. Using a non-spherical total stress tensor can inadvertently imply the presence of shear stresses in the liquid though the off-diagonal terms are solely electrostatic rather than mechanical in nature. We have added the following discussion in lines 163-204 to clarify our approach:

“In order to quantify the magnitude of the disjoining pressure in the liquid between two surfaces in close proximity, Derjaguin and Churaev [1978] used the approach of Landau and Lifshitz [1984] whereby a total stress tensor is quantified (i.e., the electrodynamic or electrostatic body forces are reduced to forces applied to the surface of a material volume, and then inserted directly into a single stress tensor). This approach of utilizing a total stress tensor arises out of the work of Maxwell [1954], whereby electric and magnetic forces on point charges were converted to continuous fields to formulate a conservation of linear momentum in terms of the divergence of the “Maxwell stress tensor” rather than in terms of the Lorentz force. Thus, the total stress tensor is the sum of the Cauchy (mechanical) stress tensor and a fictitious electrostatic (or, more generally, electromagnetic) ‘stress’ tensor. Since the total stress tensor is

anisotropic due to the non-zero off-diagonal terms originating from the electrostatic stress tensor, such an approach of using the total stress tensor may inadvertently imply shear stresses are present in the interlayer liquid between two closely spaced surfaces. Liquids such as water are generally modeled via constitutive equations that invoke sphericity of the (Cauchy) stress tensor, and shear stresses are disallowed unless the inertia is non-zero. One could argue that the nature of water (and thus its constitutive behavior) is different in tight spaces such that the material behaves more solid-like and can sustain shear stresses (see Gibbs [1878]). However, disjoining forces have been measured in aqueous solutions when the spacing between the plates is relatively large (over 100 nm) compared to the diameter of a water molecule (less than 0.5 nm). Furthermore, one could imagine a gravitational field as being analogous to an electric field as both may be expressed as a body force. As is well known, a gravitational field does not induce shear stresses in static liquids, so why should a local electric field?

In order to deal with this question, let us reconsider the experiment first described by Derjaguin involving two parallel plates being brought into close proximity in a liquid bath as shown in Figure 1 and separate the Maxwell stress tensor from the Cauchy stress tensor. Furthermore, we use Lorentz (electrostatic) force vector instead of the equivalent Maxwell stress tensor”.

5. The whole theoretical derivation is based on footnote (2): “... assume fluid in the thin film retains bulk fluid property and sufficiently far away from interfaces to neglect surface forces.” This is a critical flaw of the paper. Fig. 3b shows that the authors are dealing with disjoining pressure at film thickness of 0-30 nm separation. Many surface forces other than electrostatic force dominant in that range: van der Waals attraction, electrical double layer, hydration force, etc (Israelachvili, 2011). There is no basis to pick just the electrostatic one and neglect all others which can be arguably more dominating (i.e., the hydration force).

Surface forces other than electrostatic forces can be neglected with reasonable accuracy for pore sizes down to 10nm. We have provided an extensive discussion in lines 447-467 supporting this claim. Our analysis shown in Figure 3 and the good agreement between the modeled results and the experimental findings from literature also support that surface forces other than the electrostatic forces can be neglected without introducing significant error. We agree with you that the other surface forces can be dominant below about 10 nm and have changed the surface separation from 2 nm to 10 nm in our simulation of Figure 4. This also resolves the issue raised by another reviewer who has raised concerns about using a surface separation of 2 nm which represents lower end of the gel pores. At the surface separation of 10 nm the surface forces can be neglected without introducing significant errors. We show that the general trend of the modeled results still holds for this pore size. To avoid confusion to readers we have modified the footnote as follows:

“We assume that the liquid in the thin film retains the properties of bulk liquid and is sufficiently far away from interfaces to neglect surface forces. If one is interested in including surface forces, they can consider a separate force vector and the presumption of spherical the sphericity of the Cauchy stress tensor is still valid.”

6. Even the treatment of the electrostatic force is not rigorous. Ions and counter-ions coexist in an electrolyte solution and the presence of a charged surface will result in the well-established electrical double layer (EDL) repulsion. The authors explicitly assumed in line 267 “... non counterions are adsorbed to the surfaces ... such assumption allows us to neglect the effect of charge regulation”. This assumption basically denies EDL, which is non-physical and unfounded.

You are right that our theory fails in the event where counterions are adsorbed to the plate surfaces. We believe our treatment of electrostatic forces for the simplified case where no adsorption of counterions occurs is sound as we show very good agreement of the modeled results and experimental findings of Dubois et al. [1992] as presented in Figure 3(b). If one is to consider charge regulation, one can still do it under the framework by simply changing the boundary condition to one that satisfies the adsorption or binding of counterions to the plate surface. We have added the following text at lines 289-298 to reflect this discussion:

“If one is to consider the interaction of the charged particles with the counterions in the solution, one can still do that within the framework presented here. The derivation here can be modified to account for the adsorption or binding of counterions to the plate surface and the subsequent influence on the electric potential and electric field at the contact surface as the separation distance is reduced, allowing the existence of the Stern layer with varying thickness and the electric double layer (EDL).”

- a. The term “proper” is repeatedly used in the abstract and conclusion sections of the paper. Please define this term.

We have removed the term “proper” from the manuscript.

- b. Lorentz force is mentioned twice in abstract and conclusion. Lorentz force is the combination of electric and magnetic force on a fast-moving point charge due to electromagnetic fields. I don't see how that is relevant to this paper.

You are correct- Lorentz force has two components, the electric force and the magnetic force. The concept presented in the manuscript does not require the consideration of the magnetic force and only considers the electric force. We have mentioned this in the footnote (1) along with Equation (8) that introduces Lorentz force.

Review Round 2

Reviewer 1: Ippei MARUYAMA

I think that the authors appropriately revised the manuscript to address the reviewer's comments.

Reviewer 2: Abudushalamu AILI

My concerns have been addressed fairly, hence I recommend the publication of the manuscript.

Reviewer 3: Yida ZHANG

Thanks to the authors for addressing my comments. Most of my questions have been answered. A few more comments are below:

1. About the stress tensor of adsorbed fluid near interfaces, the authors made an analogy between the gravitational field and electric field, and thus argued that the induced stress field should be isotropic. The analogy is clear for the adopted assumption that disjoining pressure is solely generated by electric field. In general, liquid molecules in confined spaces or near another interface (whether solid-liquid or liquid-gas) are subjected to many other types of surface forces to alter their stresses. Among the many, a significant one is the hydration force that causes structural ordering of the fluid molecules near the interface. Such structurization is anisotropic by nature, giving rise to anisotropic stress ($P_T \neq P_N$) in the thin film. This difference ($P_T - P_N$) is also necessary to explain surface tension at the phase interface (Bakker equation).
2. "Disjoining forces have been measured in aqueous solutions when the spacing between the plates is relatively large (over 100 nm) ..." Please provide a few references.
3. Related to 1, I still believe that attributing disjoining pressure in CSH and eventually the drying shrinkage of cement solely to electrostatic origin is a bold oversimplification. However, the authors have clearly stated the assumptions and the range of validity of the simulation in Lines 577 to 607, which somewhat mitigated this problem.

Authors' Response

Response to Reviewer 3: Yida ZHANG

Thank you for the clarifications brought by remarks 1 and 3. Here is our response to comment 2: "Disjoining forces have been measured in aqueous solutions when the spacing between the plates is relatively large (over 100 nm) ..." Please provide a few references.

Line 188 reads:

However, disjoining forces have been measured in aqueous solutions when the spacing between the plates surfaces is relatively large (over 100 nm) compared to the diameter of a water molecule (less than 0.5 nm) [Horn et al., 1996, Pushkarova and Horn, 2005, 2008, Yaminsky et al., 2010].

References:

Horn, R. G., Bachmann, D. J., Connor, J. N., and Miklavcic, S. J. (1996). The effect of surface and hydrodynamic forces on the

shape of a fluid drop approaching a solid surface. *Journal of Physics: Condensed Matter*, 8(47):9483.

Pushkarova, R. A. and Horn, R. G. (2005). Surface forces measured between an air bubble and a solid surface in water. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 261(1):147–152.

Pushkarova, R. A. and Horn, R. G. (2008). Bubble-solid interactions in water and electrolyte solutions. *Langmuir : the ACS journal of surfaces and colloids*, 24(16).

Yaminsky, V. V., Ohnishi, S., Vogler, E. A., and Horn, R. G. (2010). Stability of aqueous films between bubbles. part 1.the effect of speed on bubble coalescence in purified water and simple electrolyte solutions. *Langmuir*,26(11):8061–8074.