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Discussions

Interactive comment on "Supercooled interfacial water in fine grained soils probed by dielectric spectroscopy" *by* A. Lorek and N. Wagner

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Reply to review 1 of the manuscript TDC-7-1441–1493-2013

We thank the reviewer for their thorough report and are pleased with the predominantly positive response. We have benefited from the insightful and constructive comments and suggestions which are of great value for us to improve the quality of the paper. We have considered the comments in a revised manuscript and appropriately responded to each reviewer's comment.

Comment 1: Page 1443. Line 24. It should read 'calorimetry'.

Response: Corrected.

Comment 2: Page 1446. Line 3. Include a full stop after ' between. In combinations.....'

Response: Corrected.

Comment 3: Page 1446. Lines 12 to 14. I understand the meaning of this statement, but it is not clear as written, ' number of ...in maximum ' ?.

Response: Corrected.

Comment 4: Page 1447-1448, lines 13 to line 25. It is always useful for readers who are going to repeat similar experiments to have units included, for each variable. They are standard units, but they would help the reader to check the equations and write computer codes for repeating the calculations.

Response: Corrected.

Comment 5: Page 1449, Lines 7 to 15. This dielectric mixing model is usually referred as the Roth's model (Roth et al., 1990). I think the correct citation should be included.

Response: Citation included.

Comment 6: Page 1450. Theory. There have been other studies not cited in this paper regarding the evaluation of adsorbed water, where the relaxation frequency of adsorbed water was measured with Nuclear Magnetic Resonance. See Figure 1 of the paper by Boyarskii et al. (2002). I included the citation below. I found several discrepancies in the data between the present paper and previously published data. For instance, Boyarskii et al. (2002) maintained that the water molecule diameter is 2.8 10ˆ-10 meters, while the authors use a value of 3.5 10ˆ-10 obtained by the work of Mohlmann (2008). Please clarify the origin of the discrepancy.

Response: Literature values of the covered surface of a water molecule vary between 0.0884 nm^2 (single molecule) and 0.19 nm^2 (molecule inside a monolayer, cf. Forsythe, 2003, Tab. 704). Hauffe and Morrison (1974) specify a weight for a monolayer of 0.26 10ˆ-6 kg/m^2. That corresponds to a covered surface/molecule of 0.115 nm^2. The di-

ameter of 0.35 nm Möhlmann (2008) results from the 0.096 nm^2/molecule (circular) (cf. Chaplin, M. 2013). Further, Maréchal (2007) mentioned an O–O distance of 0.356 nm for a Van der Waals-Complex of a water/alcohol-molecule and Agmon (1996) referred to a distance between water molecules of 0.33 nm. Based on the values for a covered surface/molecule of 0.19 nm^2 and 0.115 nm^2, a water molecule seems to need more space inside a monolayer. Therefore, a diameter of a monolayer of 0.35 nm is within the range, but values down to 0.28 nm appear also correct. We suppose that the first 1 or 2 monolayers require a different distance affected by Van der Waals forces from material surfaces than monolayers of nearly free water. This issue has to be addressed in further experimental, theoretical or numerical studies. Finally, based on the measured permittivity combined with the Birchak or CRIM-equation a thickness of 0.35 nm for a monolayer water is suggested in accordance with the study of Or and Wraith (1999).

Comment 7: Page 1452. Could the author detail how they removed low frequency electrode polarization effects in their measurement system? These effects can have serious negative effects on the dielectric measurement.

Response: The influence of electrode polarization effects was minimized (1) due to the chosen low volumetric water content and therefore a low bulk electrical conductivity of the soil and (2) with the design of the capacitance cell which has and upper electrode which is blocked by means of an defined air gap.

The blocking electrode effect in (2) was subsequently considered in the determination of the permittivity (see section 3.1 in the manuscript).

Comment 8: Page 1453, Line 9. Change und with and.

Response: Corrected.

Comment9: Pages 1455 to 1465. Results. Looking at Figure 1 of the paper by Boyarskii et al. (2002), the relaxation times at 27 degrees Celsius, with respect to the data at 20 degrees Celsius presented in this paper, differ of at least two orders of

magnitude. I understand that the soils used were different and there is a temperature difference of 7 degrees. However, in the study by Boyarskii et al. (2002), the relaxation frequency of adsorbed water for 2 monomolecular layers of water is 5 10ˆ-11 seconds, corresponding to 3.18 10ˆ9 Hz (therefore in the GHz range). In the present study for 1.53 mono layers of water and at a temperature of 19.11 Celsius, (Figure 4a, graph on the top left), there seems to be 3 relaxations: (a) a low frequency between 10ˆ2 to 10ˆ3 Hz, probably a Maxwell- Wagner effect, and (b) and (c) two high frequency relaxation occurring above 105 Hz therefore in the upper kilohertz to the megahertz range due to absorption and interfacial process. Indeed at Page 1457, Lines 25-28, The authors distinguish three relaxation processes: two weak "high frequency" processes and a strong low frequency Maxwell-Wagner effects. Clearly, there must be a strong change in relaxation frequencies over a few monolayers, making the analysis difficult, as elucidated by other authors. According to Boyarskii et al. (2002), from 1 to 2 monolayers of water the relaxation time changes of more than one order of magnitude. However, in this study the two high relaxation frequencies seems to occurs at much smaller values with respect to the study of Boyarskii et al. (2002) even at temperature above zero, and the lack of data of this study at higher frequencies prevent a clear analysis of these effects. I understand that a low temperatures, the effect of ice relaxation may shift the relaxation processes to lower frequencies since the dominant relaxation frequency for ice is in the kilohertz range, but still the difference above zero are striking. The measurement of Boyarskii et al. (2002) are performed on sandy loam and silt, therefore the differences may be due to the very different energy associated with the adsorption process.

Response: In our theoretical study (Wagner & Scheuermann, 2009) we have given a brief review of models (including the mentioned empirical equation based on NMR investigations according to Boyarskii et al., 2002) to predict the dielectric relaxation time distribution of the aqueous pore solution as a function of the distance from the particle surface. We found, that the free enthalpy of activation or Gibbs free energy of the physically bound water within the interface determined from different approaches

varies markedly. The suggested greatest upper limit of 60.8 kJ/mol is equal to the free enthalpy of activation of ice (Bockris et al. 1966) and therefore corresponds to relaxation times in the kHz-range. The suggested smallest lower limit for the first molecular water layer gives the model according to Or and Wraith (1999) with 18 kJ/mol at 293.15 K which corresponds to relaxation times in the GHz-range. The model according to Boyarskii et al. (2002) gives 20.8 kJ/mol. We have further systematically analyzed a model which relates Gibbs energy of dielectric relaxation with the appropriate soil water potential or water activity and found that it is from a theoretical point of view possible to have a broad distribution of relaxation times (kHz -GHz) in contrast to empirically proposed models such as the Boyarskii et al. (2002) equation. In this systematic theoretical analysis of the impact of a bound water contribution to the dielectric permittivity-water content relationship in comparison to experimental results we have found, that the relaxation time or Gibbs energy of activation of the bound water phase in the second molecular layer should be below 20 kJ/mol which corresponds to relaxation times according to the Boyarskii et al. (2002) equation. However, especially in case of high swelling clay mineral contents this experimental relationship can be mask by e.g. a Maxwell-Wagner processes and thus prevent the possibility of a clear analysis of the relaxation time distribution under ambient temperature-pressure conditions (see in addition Response to 10). Ishida et al. (2000) mentioned relaxation times for different clay minerals for bound water of 20 ns (Kaolinite), 8.7 ns (Montmorillonite) and 2 ns for Allophane. Montmorillonite exhibits further a Maxwell-Wagner effect with a relaxation time of 263 ns. The measurements were performed with the TDR-method and at marked higher water content as the presented study. Values of 500 to 50 ps for 1 to 2 monolayer bound water (Boyarskii et al., 2002) were not observed. We think mainly due to the difference in the investigated mineral phases (clays) and/or the used measurement methods. As the reviewer already noted, the lack of data at frequencies above 1 MHz prevents an own analysis of this effect and has to be addressed in further experiments. Against this background we analyzed the dielectric properties at extreme low water contents as well as extreme temperature conditions to suppress the

relaxation process due to free water relaxation or a direct conductivity contribution and related effects such as Maxwell-Wagner.

However, we clearly agree with the reviewer (see Comment 12): there is the need to (1) systematically analyze soils with variation in texture and structure as well as mineralogy, (2) broaden the frequency range to lower ($\sim$1 Hz) and higher frequencies ($\sim$10 GHz), (3) study the influence of the chemistry of the aqueous pore solution on the relaxation dynamics of porous materials, and thus (4) the dielectric relaxation behavior of equivalent pore solutions under defined temperature-pressure conditions.

Comment 10: Another effect that could explain the relaxation peak observed at low frequency (1 KHz) (Figure 4a, left) is the ion-dipole polarization of aqueous solutions. Often Maxwell-Wagner is provided as an explanation for a different physical effect. This effect is described by Buehler et al. (2011) and it is always almost neglected in the studies of dielectric spectroscopy of earth materials, but it can have a significant effect on low frequency measurements. It depends on the ionic-concentration of the aqueous solution and it depends solely on effect due to ions in the liquid solution. However, for frozen soil where ions are excluded from ice and concentrated into the liquid phase, this effect can play an important role, since freezing increases ion concentration in the surrounding supercooled water. Please provide information on electrical conductivity and ion concentrations of the analyzed samples, to assess the effect of ion-dipole effects on the measured relaxation peaks. If the author cannot track the paper since it is published in a conference proceeding, I would be happy to provide a copy.

Response: We decide to discuss the proposed "ion-dipole" polarization effect by Buehler et al. (2011) in a rather hypothetical but quantitative manner due to the following reasons:

(1) From our point of view, the proposed effect (related to basic theories on aqueous solutions by Falkenhangen, 1971) is, at the current stage of development of an appropriate theory not well experimental studied. Moreover, a corresponding broadband theory

including appropriate effects on the permittivity of the solution in the higher frequency range for low/high concentrations is currently not included in the study of the effect. (2) We focus in this study on the dielectric properties of interfacial water at low water contents and therefore, from our point of view, appropriate relaxation processes related to ion mobility are connected to interface processes such as the Maxwell-Wagner effect or counter ion relaxation processes. (3) The primary objective in this study is the quantification of the fluid like water content below 0 °C. Therefore, we apply our model in a frequency range in which the disturbance of the bound water relaxation process by other relaxation processes.

Comment 11: Overall, I suggest to the authors to discuss the results of Boyarskii et al. (2002) and Buehler et al. (2011), with respect to the present study, since the measured and modeled relaxation times are quite different in these studies, and they could shed light on the effect of ion-dipole effects, adsorption energy and specific surface on dielectric properties.

Response: However, especially in case of the proposed ion-dipole polarisation effect in concentrated salt solutions we cannot follow the reviewer's suggestion due to the general lack of available experimental and theoretical studies.

Comment 12: In general, for future studies, I suggest to repeat measurements at higher frequencies and also for coarser materials, since these data seem incomplete to obtain a full understanding of the processes involved. Moreover, the ion-dipole polarization should be taken into account if experimental conditions are such to determine significant effects of ion-concentrations.

Response: We fully agree with the reviewer (see Response to Comment 9).

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C924

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Please also note the supplement to this comment:

C925

http://www.the-cryosphere-discuss.net/7/C918/2013/tcd-7-C918-2013-supplement.pdf