

# Supplemental Material for:

## Screening lengths in ionic fluids

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In our work we have shown that multiple decay or screening lengths can coexist at the same time. We have used this finding to explain the structural switch in the oscillation wavelength that has recently been measured in experiments [1].

To derive our conclusions for decay lengths and the switch of structural forces, we have used the assumption of symmetry between positive and negative ions. We discussed that, if this symmetry is broken by different ion sizes, all correlation functions couple and we will not find multiple decay lengths in the asymptotic far-field limit. However, at finite range our conclusions stay valid, because simulations of asymmetric ions exhibit the same coexistence of decay lengths and oscillation frequencies. We show these additional results in Sec. I of this document.

In our work we also have shown that our theory predicts a discontinuous jump in the oscillation wavelength of the ion-ion correlations that occurs when the two leading poles have equal imaginary but different real parts. To draw a comparison between our findings and the jump observed in former experimental studies of the surface force across ion-solvent mixtures [1], we adapt the parameters of our simple model to the settings of the experiment. We perform this comparison in Sec. II.

### CONTENTS

I. Asymmetry of ions	1
II. Comparison to experimental data	2
References	4

### I. ASYMMETRY OF IONS

We have derived our conclusions on the existence of multiple coexisting decay lengths and the prediction of the structural switch in the oscillation wavelength using the assumption of symmetry between positive and negative ions. Here we show that for asymmetric ions our conclusions stay valid at finite range, because simulations of asymmetric ions exhibit the same coexistence of decay lengths and oscillation wavelengths as we have shown for the symmetric case.

In our work we investigated the decay lengths of total correlations in ionic fluids and performed Molecular Dynamics (MD) simulations for a hard-sphere ion-solvent mixture (HISM). We modeled ions (+, -) and solvents (0) as hard spheres of diameter  $d_0 = d_+ = d_- = 0.3$  nm that carry point charges  $Z_+ = -Z_- = e$  and  $Z_0 = 0$ , where  $e$  is the unit charge. We found that in HISM two different decay lengths can coexist and we replicate this result from Fig. 1 in our work in Figs. S1(a) and (b), where all particles have diameter  $d = 0.3$  nm.

We discussed that, if this symmetry is broken by different ion sizes, all correlation functions couple to each other and share the same set of poles. Thus, all correlations would decay in the same form in the asymptotic far-field limit. To test the behaviour at finite range, we performed additional simulations of asymmetric particle sizes using  $d_+ = 0.25$  nm,  $d_- = 0.3373$  nm, and  $d_0 = 0.3$  nm. These diameters are chosen such that the total volume of an ion pair is the same for the symmetric and the asymmetric system, *i.e.*,  $d_+^3 + d_-^3 = 2d^3$ . We show the results of these simulations in Figs. S1(c) and (d) together with our theoretical predictions for the symmetric system. As in the main article, Figs. S1(a) and (c) differ from (b) and (d) in the concentration of neutral particles, thus,  $\rho_0 = 10$  M in (a) and (c) and  $\rho_0 = 40$  M in (b) and (d). The concentration of ions is  $\rho = 1$  M. Lines in Figs. S1(c) and (d) represent the theoretical results of the symmetric system and are shown for comparison.

In Fig. S1 the simulations of asymmetric ions exhibit the same coexistence of decay lengths and oscillation frequencies as those of symmetric ions. Accordingly, we see that the decay lengths predicted by the HISM model are still valid

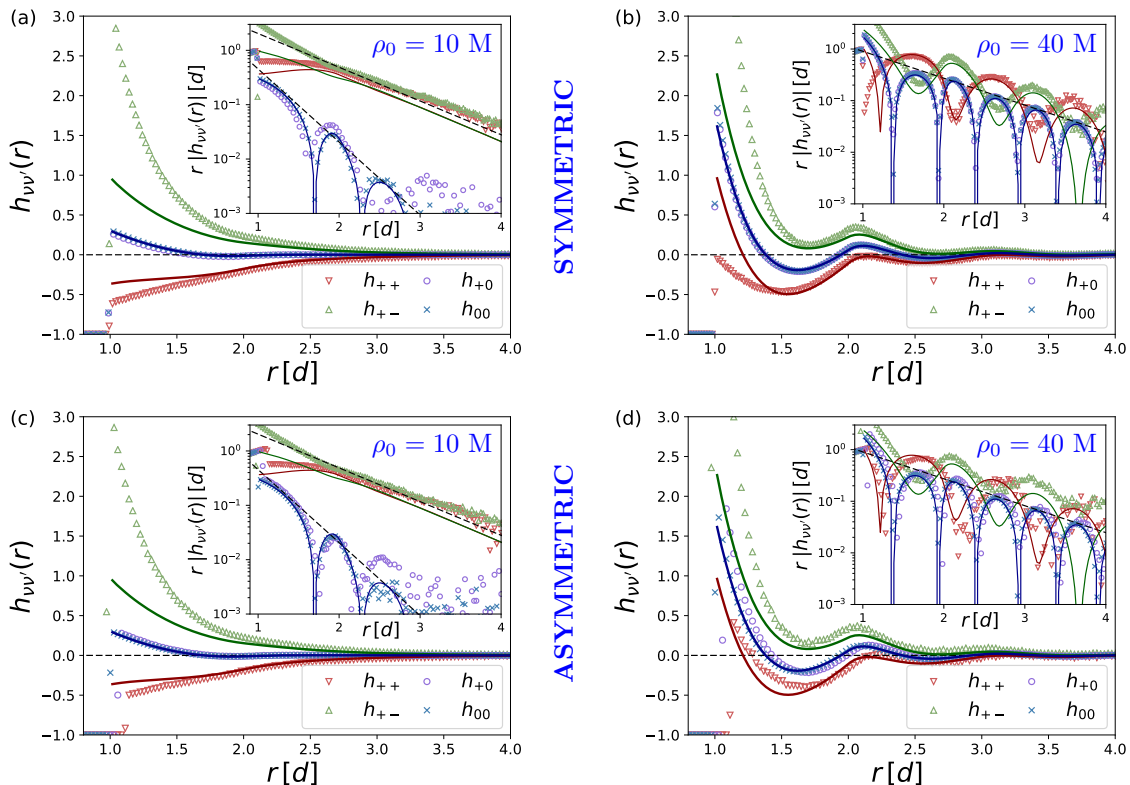


Figure S1. Total pair-correlation functions  $h_{\nu\nu'}(r)$  for ion concentration  $\rho = 1$  M and concentration of neutral particles (a),(c)  $\rho_0 = 10$  M and (b),(d)  $\rho_0 = 40$  M. Symbols represent data from MD simulations for (a),(b) the symmetric and (c),(d) the asymmetric system while lines represent data from our theory for the symmetric system. The insets show the same respective data but plotted on semi-logarithmic scale. Dashed lines in the insets represent the predicted monotonic decay  $\exp(r/\lambda_{\nu\nu'})$  with screening length  $\lambda_{\nu\nu'}$  from theory.

for asymmetric systems at (experimentally relevant) intermediate distances, *i.e.*, distances that can be accessed in experiments. Consequently, at finite range our conclusions for the symmetric system stay valid also in asymmetric systems and ion size asymmetry can be considered as a perturbation to the symmetric HISM model.

## II. COMPARISON TO EXPERIMENTAL DATA

In this section we draw a direct comparison between the predictions of our theory and the discontinuous jump in the oscillation wavelength of the ion-ion decay as it was measured in experimental studies of the surface force across ion-solvent mixtures [1]. First, we simulated the experimental system using the HISM model with asymmetry between ion and solvent sizes in order to validate the HISM model. Second, we compare the density functional theory for the symmetric HISM model with simulations and experiments.

In the experiments [1], electrolyte solutions are prepared from the ionic liquid 1-butyl-1-methylpyrrolidinium bis[(trifluoromethane)sulfonyl]imide,  $[C_4C_1\text{Pyrr}][\text{NTf}_2]$ , and from propylene carbonate as a solvent. The experiments have been interpreted using an ionic diameter  $d_+ = d_- = 0.4$  nm and a solvent diameter  $d_0 = 0.5$  nm [2], where this ionic diameter also agrees with other works [3, 4]. For propylene carbonate solvent molecules diffraction measurements in combination with Molecular Dynamics (MD) simulations have shown a first peak in the total pair correlations that corresponds to a size of approximately 0.53 nm [5] rather than 0.5 nm. The dielectric constant of the system has been reported to vary between approximately 64 for pure solvent and approximately 14 for pure ions [2]; these values relate to Bjerrum lengths of 0.87 nm and approximately 4.5 nm. Furthermore, for the experiment, the concentration of the pure ionic system has been reported with  $\rho_+ = \rho_- = 3.3$  M while the concentration of pure solvent is  $\rho_0 \approx 12$  M. Concentrations for different compositions in the experiment are listed in Table S1, where the solvent concentration approximately changes linearly with the ion concentration when the composition is changed from pure solvent to pure ions. When both solvent particles and ions are modeled as (charged) hard spheres of diameters  $d_0 = 0.5$  nm and

Table S1. Parameters used in our simulations, following the data reported in Ref. [2].

$\rho$	$\rho_0$	$\lambda_B$
0.01 M	11.85 M	0.87 nm
1 M	9 M	1.27 nm
2 M	4.7 M	2.06 nm
2.5 M	3.06 M	2.79 nm
3 M	1 M	3.98 nm
3.3 M	0 M	4.46 nm

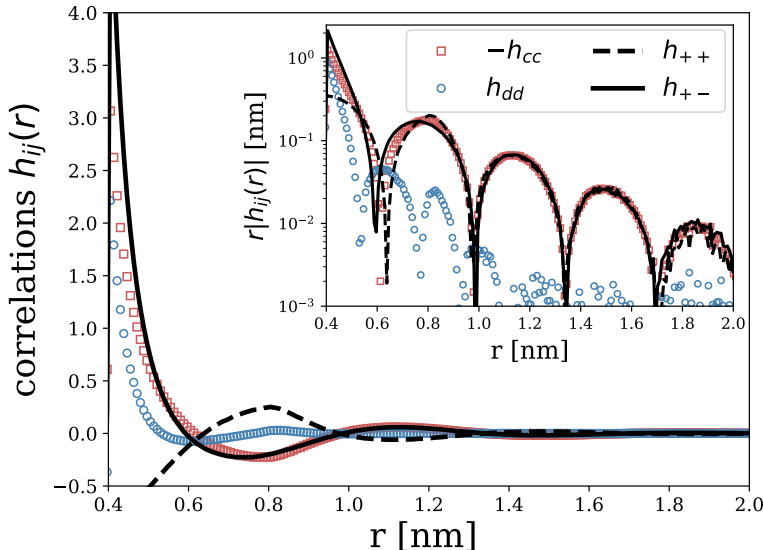


Figure S2. Pair correlations  $h_{ij}(r)$  in a restricted primitive model system obtained from MD simulations for a concentration  $\rho = 3.3$  M, an ionic diameter  $d = 0.4$  nm, and a Bjerrum length  $\lambda_B = 4.46$  nm. The inset shows the data multiplied by  $r$  using a logarithmic  $y$  axis. The wavelength of the shown large oscillations is approximately 0.71 nm.

$d_+ = d_- = 0.4$  nm, the total volume fraction  $\eta = \frac{\pi}{6}(d_+^3\rho_+ + d_-^3\rho_- + d_0^3\rho_0)$  is maximal for pure solvent with  $\eta \approx 0.47$ . This value is still smaller than 0.49, where fluid-solid phase coexistence sets in for monodisperse hard spheres [6]. Note that hard spheres with a larger diameter of 0.53 nm would not form a stable liquid phase.

First, we simulated the experimental system using hard-sphere ions of diameter  $d_+ = d_- = 0.4$  nm and hard-sphere solvent particles of diameter  $d_0 = 0.5$  nm. In Fig. S2 we plot the correlations of a pure ionic system, *i.e.*, a restricted primitive model with  $d = 0.4$  nm and concentration  $\rho = 3.3$  M. According to the experimental data listed in Table S1, we used a Bjerrum length  $\lambda_B = 4.46$  nm. The oscillation wavelength of the shown charge-charge correlations is approximately 0.71 nm.

In Fig. S3 we show results from our simulations for all compositions listed in Table S1. The simulation results in Fig. S3 agree well with the experimental data and confirm the HISM model with solely steric and Coulombic interactions as sufficient to describe the experimentally observed rapid switch of the wavelength [1].

Next, we compare the predictions of our theory with the experimental data. In our work we developed a theory for equally sized particles only. Thus, to compare theory with experiment, we have chosen one single diameter  $d = d_+ = d_- = d_0 = 0.4$  nm for all particles. We fixed the Bjerrum length to  $\lambda_B = 0.87$  nm to avoid divergent behaviour of our theory at low permittivities or respective large Bjerrum lengths. We have taken the total volume fraction constant, *i.e.*, the average amount of particles did not change during varying the ion concentration such that for increasing ion concentration the solvent concentration decreased. We account for the space filling nature of the solvent by fixing the volume fraction to values of around  $\eta = 0.47$ , *i.e.*, the volume fraction of the pure hard-sphere solvent we previously discussed, but as our analytical theory is derived for symmetric systems, we take the solvent diameter to be 0.4 nm as well. However, the oscillation wavelength at low ion concentrations, *i.e.*, for values  $\rho \leq 2.5$  M in Fig. S3, is dominated by the density-density correlations of the system and, thus, related to the particle diameter in our theory. At low ion concentration, however, most particles in the system are solvent particles which, according to our previous discussion, should be considered with a size of 0.53 nm rather than 0.4 nm. Consequently, the oscillation wavelength should be related to the size 0.53 nm measured in propylene carbonate and not to the size  $d = 0.4$  nm

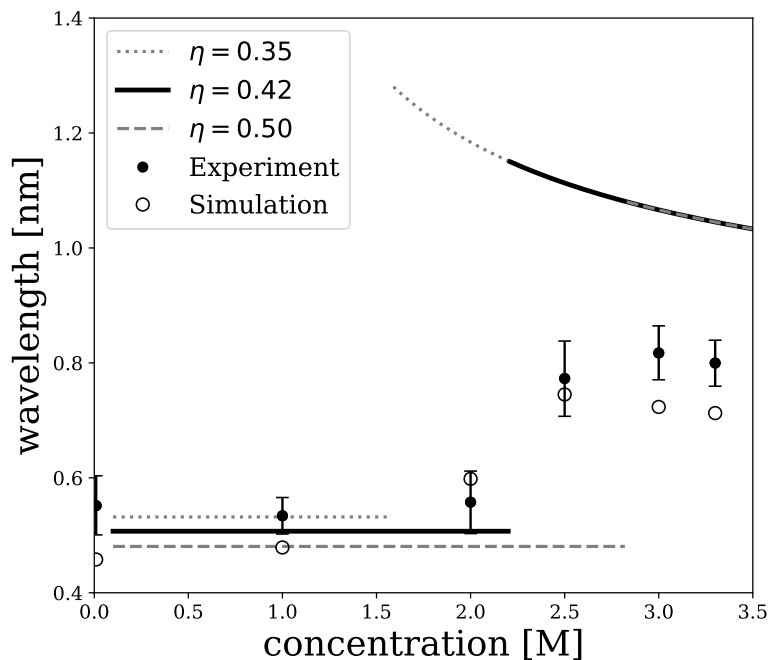


Figure S3. Oscillation wavelength of the ion-ion decay length as a function of ion concentration  $\rho$ . Open symbols represent our simulation results, where we took  $d = d_+ = d_- = 0.4$  nm,  $d_0 = 0.5$  nm, and concentrations and Bjerrum length as listed in Table S1 and explained in the text. Full symbols show experimental data taken from Ref. [1] including error bars. Lines are obtained from theory using a diameter  $d = d_+ = d_- = d_0 = 0.4$  nm and a fixed total volume fraction as mentioned. Note that wavelengths are rescaled at low ion concentrations as discussed in the text.

that we used as a diameter in the symmetric theory.

In Fig. S3 we show the predicted oscillation wavelength from our theory in comparison to our simulations and the experimental results from Ref. [1]. We performed our calculations for three different total volume fractions of the hard particles in our model, where the values 0.42 and 0.5 are closest to the previously discussed volume fraction 0.47 of a pure solvent. According to our previous discussion on the oscillation wavelength, we have rescaled the wavelength at low concentrations (smaller than the concentration at the jump) by the factor  $0.53/0.4$  to adapt it to the size of solvent molecules in the experiment. We see that the resulting theoretical curves in Fig. S3 agree well with the experimental data at low ion concentrations. At high ion concentrations, the theoretically predicted wavelength is significantly larger than the experimentally measured wavelength. In our studies we observed that changing the dielectric constant has an influence on the value of the wavelength, but at high ion concentrations the predicted screening length that corresponds to the wavelength diverges. As a result the position of the predicted jump would shift, too. However, this divergence is not reflected in our simulations and, accordingly, it arises from the missing ingredients in our simplified theory.

In conclusion, our theory in combination with a very simple model system can predict the correct position of the jump and the correct value of the smaller wavelength in the experimental data. By discussing additional simulations, we argued that the overestimation of the larger wavelength is an artifact from missing components in our theory. The general theory including the correct contribution  $c^{\text{corr}}$  (*i.e.*, having a correct functional) does not make any additional assumptions compared to the simulation and would be expected to recover the simulation results.

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