

# Casimir Effect: Theory and Applications

## Summer school lectures

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### (a) Electrostatics and dispersion interactions in bulk electrolytes

An investigation of the decay behaviour of electrostatic potential and distribution functions as functions of distance gives important insights into properties of ionic fluids. The asymptotic decay of these entities can quite often give good estimates for surprisingly short distances. The mean electrostatic potential from an ion and the pair distribution functions (radial distribution functions) in low density electrolytes decay for large distances  $r$  like a Yukawa function  $\exp(-r/L)/r$ . The decay length  $L$  is approximately equal to the Debye length, which is the decay length given by the Poisson-Boltzmann approximation where pair distributions between an ion and the surrounding ions are obtained by ignoring the correlations among the latter. The exponential decay originates from the screening of the Coulomb interactions caused by the arrangement of ions around each ion.

At higher densities the decay length deviates from the Debye length and another term that decays like a Yukawa function with a different decay length also becomes important in the pair distribution function. At even higher densities the two Yukawa terms merge and turn into an oscillatory term. The oscillatory behaviour is typical for molten salts, but exists also for less dense systems. Oscillatory and monotonic decay terms can exist simultaneously and, depending on the circumstances, one or the other dominates for large  $r$ . In general, the average charge distribution around each ion and the mean electrostatic potential due to the ion also decay in the same fashion with the same decay lengths and, for oscillatory cases, same wave lengths as the distribution functions.

In the presence of dispersion interactions between the ions, the pair distributions decay instead like a power law for large  $r$ . Exponentially decaying terms are still present, but when  $r$  is increased they are eventually dominated by power law contributions that decay slower with  $r$ . The leading power law term is the same as in liquids of electroneutral particles. The dispersion and electrostatic interactions are, however, coupled to each other, which makes the electrostatic potential and the charge distributions around each ion to decay like power laws too for large  $r$ . The leading term is independent of the sign of the ionic charge, a feature that is caused by a separation of charge far from the ion caused solely by the dispersion interactions.

### (b) Surface interactions in electrolyte systems

Salient features of the interaction forces between surfaces in electrolyte systems are presented, both for surfaces in contact with ionic fluids and surfaces solely covered by laterally mobile ions. In all cases, the surface force contribution caused by electrostatic correlations between the ions is prominent – in the latter case it gives the thermal Casimir force. For surfaces in contact with ionic fluids other contributions to the surface interactions

may, however, dominate, like the ideal pressure term that is proportional to the total ion density at the plane where the surface forces are evaluated (for two equal surfaces usually the midplane between the surfaces). The latter is the only contribution to the force that is included in the Poisson-Boltzmann (PB) approximation, where ion-ion correlations are ignored. These correlations can cause large deviations from the PB prediction both because the electrostatic correlation contribution to the force is missing in the PB approximation and since correlations can have large influences on the ion distribution between the surfaces.

The zero frequency (static) contribution to the van der Waals (vdW) interactions between the walls behind the surfaces is screened by the electrolyte in all cases, but in order to obtain this effect it is paramount to include the correlation interactions due to the surface polarisations caused by the ions – the so-called image charge interactions – on the pair correlation level. The images give rise to a contribution that exactly cancels the zero frequency vdW contribution. The screening is particularly important for hydrocarbon/water systems, where this contribution constitute a large part of the total vdW interaction in absence of ions.

Dispersion interactions between the ions and the walls give rise to a further contribution to the surface force. Such interactions can also have quite large influence on the ion distribution between the surfaces, causing an indirect effect on the surface force, for instance via the the ideal pressure term. Since the dispersion interaction depends on the polarisability of the ions, which can vary a lot between different ions (most notably anions), this constitutes an important reason for ion specificity.