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Summary

Effective interactions between objects immersed in a fluid media or between surfaces confining the fluid play a central role in soft matter, especially in colloidal suspensions, and in biological systems. One example of these interactions is called critical Casimir force. It may appear in a binary mixture close to the critical demixing point, and in this case is induced by long-range concentration fluctuations. Depending on the properties of the confining surfaces, the force can be repulsive or attractive; attraction is predicted for uncharged surfaces preferentially adsorbing the same component, whereas uncharged surfaces with different adsorption preferences repel each other. Since the magnitude and the sign of the critical Casimir forces can be controlled by small temperature changes and by surface treatments, recently this field of research attracts increasing attention.

The theory of critical Casimir forces for uncharged surfaces and for mixtures of neutral components has been established theoretically well. However, in colloidal systems the surfaces of the colloidal particles are often charged. Moreover, many relevant fluid media contain polar liquids such as water, which can dissociate into ions due to the presence of the charged surfaces. Interactions between charged surfaces immersed in non-critical fluids are described by the Debye-Hückel (DH) theory. However, when the binary solvent is close to the critical demixing point and the ions are soluble only in one of the solvent components (typically water), distribution of ions and the solvent components near the charged and selective surfaces influence each other. As a result, the measured interactions deviate significantly from the sum of the Casimir and electrostatic potential in the DH approximation [*Phys. Rev. E* **80**, 061143 (2009)]. In some cases instead of repulsion, expected from the sum of the Casimir and electrostatic potentials, attraction was measured [*Soft Matter* **7**, 5360 (2011)]. The purpose of the thesis is theoretical explanation of the experimental results.

In order to fulfill this purpose, we develop a Ginzburg-Landau-type theory for a binary mixture containing ionic solutes, confined by charged selective surfaces. We take into

account critical phenomena and the electrostatic forces. The Ginzburg-Landau functional is derived from the microscopic description. The analytical results are obtained by minimizing the approximate functional. Order parameter and charge density profiles as well as the effective interactions between the confining surfaces are calculated in the case of chemical preference of ions for one of the solvent components.

The analytical investigations contain two main parts. In the first part, our calculations are based on the approximation scheme valid if the bulk correlation length of a solvent is much larger than the Debye screening length; in this critical regime the effect of charge on the concentration profiles of the solvent is subdominant. Such conditions are met in the recent measurements of the effective forces acting between a substrate and a spherical colloidal particle immersed in the near-critical water-lutidine mixture [*Nature* **451**, 172 (2008)]. We show that the preferential solubility of ions in water leads to the modification of the charge density profiles in respect to the ones obtained from the DH theory. Our analytical results are in a quantitative agreement with the experimental ones.

In the next part of the analytical investigations, we focus on the range where the electrostatic screening length is larger than the correlation length. For this case, we show that hydrophilic ions present in the mixture can lead to an attraction between like charge surfaces with opposing preferential adsorption of the two species of the mixture, even though the corresponding Casimir potential in uncharged systems is repulsive. This prediction agrees with recent experiments [*Soft Matter* **7**, 5360 (2011)]. We also show that oppositely charged hydrophobic surfaces can repel each other, although the Casimir potential between uncharged surfaces with like preferential adsorption (selectivity) is attractive. This behavior is expected when one of the confining surfaces is strongly selective and weakly charged, whereas the other confining surface is weakly selective and strongly charged. The Casimir potential can change sign because the hydrophilic ions near the weakly hydrophobic surface can overcompensate the effect of hydrophobicity, and this surface can act as a hydrophilic one. We also predict a more attractive interaction between hydrophilic surfaces and a more repulsive interaction between hydrophobic surfaces than given by the sum of the Casimir and DH potentials.

In addition to analytical investigations of the approximate form of the Ginzburg-Landau functional, we solve numerically the obtained Euler-Lagrange equations following from the minimization of the functional. The numerical solutions confirm the analytical

results. Moreover, within the numerical solutions, we are able to investigate the effective potential between the objects for a whole range of the correlation and Debye-screening lengths. We predict new cases of effective potentials between the objects which have not been examined experimentally so far.

The majority of the results have been published in the following papers:

1. F. Pousaneh, A. Ciach,
The origin of the attraction between like charged hydrophobic and hydrophilic walls confining a near-critical binary aqueous mixture with ions,
J. Phys.:Cond. Mat. **23**, 41201 (2011). (Chapter 5,7)
2. F. Pousaneh, A. Ciach, and A. Maciołek,
Effect of ions on confined near-critical binary aqueous mixture,
Soft Matter **8**, 3567 (2012). (Chapter 5,6)
3. F. Pousaneh, A. Ciach, and A. Maciołek,
How ions in solution can change the sign of the critical Casimir potential,
Soft Matter: DOI:10.1039/C3SM51972D (2013). (Chapter 5,7,8)