Séminaire

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Amphithéâtre Henri Benoît

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The Long-Range Attraction between Hydrophobic Macroscopic Surfaces

The origin and nature of the interaction between hydrophobic macroscopic substrates across water and aqueous solutions[1] has been in debate for the last 40 years.[2] Here, atomically smooth mica surfaces are rendered hydrophobic and charge neutral by immersion in cationic surfactant solutions at low concentrations. Lateral correlations along the hydrophobic surfaces whose separation can be varied continuously down to contact are measured by x-ray scattering using a modified Surface Force Apparatus (SFA) coupled with synchrotron radiation, named SFAX. Upon intersurface variation, the evolution of the scattering patterns codes for a redistribution of counterions[3] mediated by the microstructuration[4] of the adsorbed film. This key mechanism to the long-range attraction between similar, overall charge-neutral walls, is generalized to the three main categories of substrates rendered hydrophobic, namely surfaces obtained with surfactant monolayers physically adsorbed from solution to deposited ones, and substrates coated with a hydrophobizing agent bonded chemically onto the surface. The interaction energy scales as $A \exp(-2\kappa D) / 2\kappa D$ at large separations[3,5] with measured decay lengths in accord with theoretical predictions, simply being half the Debye screening length, $\kappa^{-1}/2$. Taken together with the prefactor A scaling as the ionic strength, the interaction energy is demonstrated to have an *electrostatic* origin in all the systems. The adsorption or desorption of pairs of positive and negative ions on small islands along the interface from the electrolyte solution, the fluctuation of the surface charge density around a zero mean-value, the correlations in the local surface ion concentrations, the redistribution of counterions upon intersurface variation, all contribute and are tuned finely by the inhomogeneities and defects present in the hydrophobic layers. It appears that the magnitude of the interacting energy can be described by a single master curve encompassing all the systems.[6]

[1] Blake, T.D.; Kitchener, J.A. *J. Chem. Soc. Faraday Trans. I* **1972**, *68*, 1435-1442.

[2] Meyer, E.E.; Rosenberg, K.J.; Israelachvili, J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15739-15746.

[3] Kékicheff, P.; Iss, J.; Fontaine, P.; Johner, A. *Phys. Rev. Lett.* **2018**, *120*, 118001.

[4] Kékicheff, P.; Contal, C. *Langmuir* **2019**, *35*, 3087-3107.

[5] Kékicheff, P.; Spalla, O. *Phys. Rev. Lett.* **1995**, *75*, 1851-1854.

[6] Kékicheff, P. *Adv. Colloid Interface Sci.* **2019**, *270*, 191-215.

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