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Electric Double Layers in Aqueous and Oily Solvents: Thermodynamic Cycles, Surface Heterogeneities, and Charge Regulation

After a quick general overview of the basic physics of electrostatic screening of charged surfaces in an electrolyte, we will discuss some of our recent theoretical work in this field. We will start with a thermodynamic analysis [1] of Brogioli's capacitive device [2] to harvest "blue" energy out of the mixing of river and sea water the (free) energy involved is equivalent to a waterfall of about 200 meter and hence this energy is economically interesting, especially for countries with river deltas. Brogioli's device cyclically charges and discharges porous electrodes immersed in sea and river water, respectively, and is based on the expansion and compression of the double layer in fresh and salty water. We will show that Brogioli's device can be seen as an analogue of a Stirling heat engine, and we propose a modification to construct the most efficient "blue engine" based on a Carnot-like cycle [1]. The surface potential of the porous electrodes, up to $\sim 1V$, exceeds the thermal voltage ($\sim 25mV$) by far, which causes ordinary Poisson-Boltzmann (PB) theory to break down, even for monovalent ions in water. The Stern layer and other ion-specific effects become relevant in this regime, and we will discuss an extension of PB theory in which the "polarisability holes" due to the poorly polarizable ions compared to water are taken into account, giving good agreement with experimental measurements of differential capacities without any fit parameter.

We will then address some recent work on screening ions and colloidal suspensions in oily solvents [3,4], where Bjerrum pair formation takes place [3] and where the colloidal charge is strongly regulated and depends on the thermodynamic state [4]. The latter gives rise to re-entrant melting in agreement with recent experiments, and to heterogeneous surface charge distributions in the nonspherical geometry of Wigner-Seitz cells of face-centered-cubic and body-centered-cubic crystalline states. In this context we will also briefly discuss a numerical technique that we developed to explicitly calculate the double layer structure of heterogeneously charged surfaces [5,6].

[1] N. Boon and R. van Roij, *Mol. Phys.* **109**, 1229 (2011)

[2] D. Brogioli, *Phys. Rev. Lett.* **103**, 058501 (2009).

[3] C. Valeriani, P. Camp, J. Zwanikken, R. van Roij, and M. Dijkstra, *Soft Matter* **6**, 2793 (2010).

[4] F. Smalenburg, N. Boon, M. Kater, M. Dijkstra and R. van Roij, *J. Chem. Phys.* **134**, 074505 (2011).

[5] N. Boon and R. van Roij, *J. Chem. Phys.* **134**, 054706 (2011);

[6] N. Boon, E. Carvajal Gallardo, S. Zheng, E. Eggen, M. Dijkstra, and R. van Roij, *J. Phys.: Condens. Matter* **22** 104104 (2010).

REFRESHMENTS WILL BE SERVED

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