

Contact theorems for charge and density profiles of ionic fluids on the charged surface

M. Holovko^a, J.-P. Badiali^b and D. di Caprio^b

^a*Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*

^b*Laboratoire d'Electrochimie, Chimie des Interfaces et Modélisation pour l'Energie, ENSCP, CNRS, Université P. et M. Curie, France*

By the direct integration BBGKY equation between singlet and binary distribution functions of ionic fluid in the presence of charge surface the exact relations (so-called contact theorems) for the contact values of charge and density profiles are obtained [1]. The obtained results are analyzed for symmetrical [2] and nonsymmetrical [3,4] ionic systems. For the electrolytes with a single type of cation and anion, the contact value of charge profiles can be presented as the sum of three contributions. One of them is the normal component of the Maxwell electrostatic stress tensor. The second one is the surface electrostatic property, which is defined as the integral of product of the gradient of the electrical potential and the density distribution function of coions. The third term is the bulk contribution, which is defined by the sum for anions and for cations of the product of their charge and their partial pressure. For noncharged surface, only the last two terms are present and have the same sign in the case of size asymmetry. In the case of charge asymmetry, the contact value of the charge profile is the result of the competitions of bulk and surface terms in which the bulk term is dominant. Using both the contact theorems for the density and the charge profiles, the exact expressions for the contact values of the profiles of coions and counterions are obtained and some related properties are discussed. A semiempirical expression of the contact value of the charge profile is discussed in relation to exact result. Within a field theoretical description, the phenomenon of spontaneous polarization of a neutral hard planar interface for valence asymmetric ionic fluids is discussed. The theoretical results are compared with numerical simulations data and are shown to be in very good agreement.

1. M. Holovko, J.-P. Badiali, D. di Caprio, *J. Chem. Phys.*, **123**, 234705 (2005)
2. M. Holovko, J.-P. Badiali, D. di Caprio, *J. Chem. Phys.*, **127**, 014106 (2006); **128**, 117102 (2008)
3. M. Holovko, D. di Caprio, *J. Chem. Phys.*, **128**, 174702 (2008)
4. D. di Caprio, M. Holovko, *J. Phys. Chem. B*, **113**, 2006 (2009)