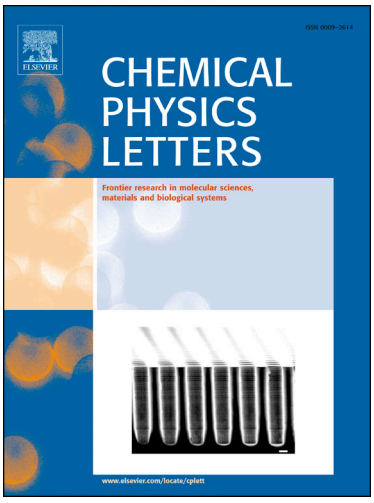

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Spontaneous ordering at the free surface of molecular clusters

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Abstract

The present paper seeks to establish a theoretical framework to account for the spontaneous molecular ordering at free surfaces of molecular aggregates. It is shown that within a multipole representation of the molecular interactions, ordering is the effect of the interplay of two fundamental causes: the translational symmetry breaking of the bulk phase at the interface and the interactions of multipoles of different parity. Quantitative analysis of the *order parameter* demonstrates building up of ordering at different length scales with range depending on the strength of the interactions.

Keywords: Surface ordering, polarity formation, multipole, molecular dynamics

Most phenomena occurring at the interface of a thermodynamic system are driven by the electric charges located therein, or more generally, by the molecular ordering occurring at the boundary layer. This is, for instance, the case of phenomena such as adhesion, lubrication, catalysis, and biomembrane function [1]. Consequently, it is of great importance to understand the details of the surface charge distribution and to unravel the microscopic mechanics generating cooperative effects. By surface ordering we mean here any microscopic ordering at the surface able to produce a net charge accumulation. We thus exclude situations where dipoles align parallel to the free surface. In this respect the

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