Instabilities with respect to periodic ordering in primitive models of ionic fluids

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As is shown by the mean-field analysis [1], the primitive model (PM) of ionic systems undergos an instability with respect to periodic ordering in addition to a gas-liquid-like separation. This instability can be identified with the structural line indicating pre-transitional effects.

In this work, we study the effects of size and charge asymmetry on the periodic ordering in the PM using the collective variables based theory [2]. As in [1], we consider the three regimes of size asymmetry: small size asymmetry, moderate and large size asymmetry, and very large size and charge asymmetry. We extend previous studies in two ways. First, we employ a non-local density approximation for the reference hard sphere fluid which leads to the Percus-Yevick pair direct correlation functions for the uniform case [3]. Second, we use the Weeks-Chandler-Anderson regularization scheme [4] for the Coulomb potential inside the hard core.

Following the ideas of [5], we determine the relevant order parameter connected with the periodic ordering and analyze the character of the dominant fluctuations along the structural lines. We show that the above-mentioned modifications produce quantitative and partly qualitative changes in the phase diagrams obtained previously.

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