FLUCTUATIONS AND SELF-ORGANIZATION PHENOMENA IN SYSTEMS WITH COMPETING ATTRACTIVE AND REPULSIVE FORCES

L. Reatto, A. Imperio[1], A. Parola[2], D. Pini[1]

[1]*Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica, Università di Milano, Via Celoria 16, Milano, Italy*

[2]*Istituto Nazionale di Fisica della Materia and Dipartimento di Scienze Fisiche, Università dell'Insubria, Via Valleggio 11, Como, Italy*

Fluids where the attractive interaction at distances slightly larger than the particle size is dominated at longer distance by a repulsive contribution, undergo deep modifications in their phase behavior with respect to the simpler, purely attractive case. Above a certain strength of the repulsion, bulk liquid-vapor separation is inhibited because of its high energetic cost, and replaced by a transition to nonhomogeneous phases where the particles form bubble- or stripe-like domains. Even for weaker repulsions, such that the liquid-vapor transition is still present, the competition between attraction and repulsion strongly affects the phase portrait of the fluid, causing a remarkable flattening of the liquid-vapor coexistence curve.

We complete a previous investigation of this homogeneous regime based on the self-consistent Ornstein-Zernike approximation (SCOZA) by studying the stability of the liquid-vapor transition with respect to the fluid-solid one. We find that the range of the attraction at which liquid-vapor phase separation becomes metastable with respect to freezing is appreciably larger than in systems with purely attractive interactions, and that the correlations in the neighborhood of the liquidus line behave quite differently in the two cases. Moreover, the large density fluctuations that occur near the (metastable) liquid-vapor critical point are greatly enhanced by the competition between attractive and repulsive forces, and this leads to a dramatic decrease of the interfacial free energy for fluid-solid nucleation. Such an effect is much more pronounced than that observed for narrow attractive interactions.

We then turn to the inhomogeneous regime, which we study by means of Monte Carlo simulations in two-dimensional systems. The results for the structure factor and the radial distribution function carry the signature of the two different lengthscales that govern the intra- and inter-cluster correlations. We also consider the boundary between the homogeneous and the density-modulated fluid and, within the latter, the bubble-stripe transition which takes place as the density is increased. The main features of this transition can be described, although only qualitatively, by means of simple mean-field expressions for the energy of different particle arrangements.

Finally, we employ simulations in the two-dimensional case to investigate the response of the homogeneous fluid to an external periodic potential. Because of the occurrence of strong density fluctuations even in the homogeneous regime, we expect that, by suitably tuning the wavelength of the perturbation, one can induce a strong response in the fluid.