Effective Hamiltonian for Liquid-Vapor Interfaces

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Two types of fluctuations, which require both the same careful statistical analysis, occur simultaneously at fluid interfaces: capillary waves of the interface position and fluctuations in the bulk, the latter being also present in the absence of an interface. The structural properties of fluid interfaces are still unresolved due to the dearth of rigorous theoretical results for realistic systems.

Starting from a microscopic density functional theory for inhomogeneous fluids we derive an effective Hamiltonian for liquid-vapor interfaces of simple fluids that goes beyond the common phenomenological capillary-wave description. Explicit expressions for the surface tension and the bending rigidities of capillary waves of fluid interfaces are given. In contrast to other approaches we take into account the long-ranged power-law decay of the dispersion forces between the fluid particles, which changes qualitatively the functional form of the wavevector-dependent surface tension. In particular, we find two different limiting bending rigidities for the capillary waves, a negative one for small wavevectors determined by the long-ranged dispersion forces and a positive rigidity for large wavevectors due to the distortions of the intrinsic density profile in the vicinity of the locally curved interface. The relevance of these results to the interpretation of scattering experiments and the differences between our approach and the standard capillary-wave theory are discussed. We expect that the prediction of a negative bending rigidity can be confirmed by X-ray scattering experiments.