

# Capillary waves and the decay of density correlations at liquid surfaces

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In 1976 Wertheim predicted strong density-density correlations at free liquid surfaces, produced by the capillary wave fluctuations of the interface. That prediction has been used to search for a link between Capillary Wave (CW) theory and Density Functional (DF) formalism for classical fluids. Recent works[1, 2] have analysed the decaying tails of these CW effects moving away from the interface, as a clue for the extended CW theory, beyond the strict long wavelength limit studied by Wertheim. From these works[1, 2] some apparently fundamental inconsistencies between the CW and the DF theoretical views of the fluid interfaces arose from the asymptotic analysis of the CW signal.

To clarify the CW-DF link and explain those apparent contradictions we propose a novel route[3] to separate local non-CW surface correlation effects of truly non-local propagation of the CW fluctuations from the surface towards the liquid bulk. This is performed introducing an inhomogeneity in the Ornstein-Zernike equation:

$$[-b\partial_z^2 + bq^2 + \Phi''(\rho(z))] \hat{S}_b(z, q) = 1 + R(z, q),$$

being  $q$  the wavevector modulus and  $\hat{S}_b(z, q)$  represent non-CW surface correlation effects, hence, CW fluctuations are given by:

$$[-b\partial_z^2 + bq^2 + \Phi''(\rho(z))] \Delta\hat{S}_b(z, q) = R(z, q).$$

Consequently, as square gradient approximation is licit in long wavelength regime we can suppose that every finite size  $R(z, q)$  function can be seen as a Dirac delta function centered in the surface. Results are shown in Figure 1. In panel (c)  $\Delta\hat{S}(z, q)$  shows non-local propagation of CW fluctuations  $e^{-\kappa_{1,q}z}$ , being  $\kappa_{1,q} = \sqrt{\kappa_{1,0}^2 + q^2}$ .

Those results allow us to conclude that with this proposal, coherent results are obtained and inconsistencies between CW and DF are not observed as in recent works. However,  $R(z, q)$  has to be generalised in order to apply further than in square gradient approximation, i.e  $R(z, q)$  can not be used as a Dirac delta function. In this regime, a function  $R(z, q)$  related with equilibrium profile and thermodynamic functions must be used.

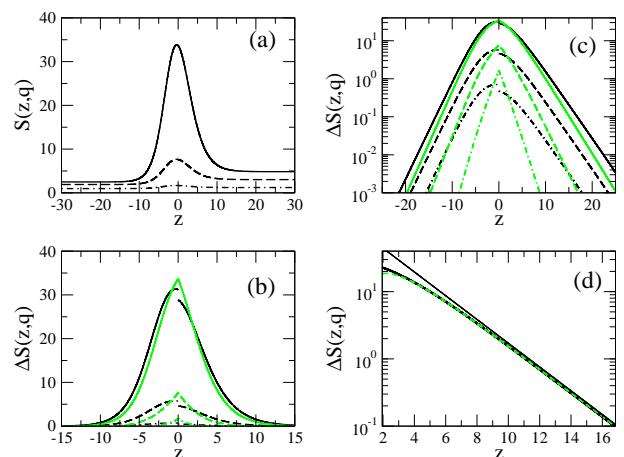


Figure 1: The local structure factor in the liquid-gas interface of a LJ model at  $T/T_c = 0.87$ , for different values of the wavevector using the LJ distance parameter as unit for  $z$  and  $q$ . Panel (a): Total  $S(z, q)$ , for  $q = 0.2$  (full line),  $q = 0.4$  (dashed line) and  $q = 0.8$  (dash-dotted line). Panels (b) and (c): The CW contributions  $\Delta S(z, q) = S(z, q) - S_{bulk}(q)$  (black lines) and  $\Delta\hat{S}(z, q)$  (grey, online red lines). Panel (d)  $\Delta S(z, q)$ , in log-scale for the liquid branch with  $q = 0.2$ , to show the dominant decaying tail  $e^{-\kappa_{1,0}z}$  (thin line) local non-CW surface correlation effect, and the best fit contribution from the next decaying terms  $e^{-\kappa_{1,q}z}$  non-local propagation of CW fluctuations and  $e^{-2\kappa_{1,0}z}$ .

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