Thermal capillary waves in colloid-polymer mixtures - static and dynamic correlation functions

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At rest, the free interface between any two fluids appears to be smooth. However, due to the thermal energy $k_B T$, all fluid interfaces are corrugated and these fluctuations are suppressed by the interfacial tension (γ) and gravity. This leads to a mean square amplitude h_q of each Fourier mode q: $\left\langle |h_q|^2 \right\rangle = \frac{k_B T/L^2}{\gamma\left(q^2+L_c^{-2}\right)}$, with L the system size and L_c the capillary length. Furthermore, each mode is damped exponentially with a decay rate of $\omega_q = \left(qL_c + \frac{1}{qL_c}\right)\gamma/\left(2\eta L_c\right)$, where η is the sum of the viscosities of the two fluid phases.

The interface fluctuations can be observed experimentally in phase separated colloid-polymer mixtures by means of laser scanning confocal microscopy. This allows us to construct real space height-height correlation functions, either statically or dynamically, from a 1D cut through our 2D interface. From the theoretical expressions in Fourier space it is possible to obtain the theoretical correlation functions: the static correlation $g_h\left(x\right) = \left\langle h\left(x',t'\right) h\left(x'+x,t'\right)\right\rangle = \frac{k_B T}{2\pi\gamma} K_0\left(x/L_c\right)$ and the dynamic correlation $g_h\left(t\right) = \left\langle h\left(x',t'\right) h\left(x',t'+t\right)\right\rangle = \frac{k_B T}{2\pi\gamma} K_0\left(t/\tau\right)$, with K_0 the modified Bessel function of the second kind and the capillary time $\tau = \frac{\eta L_c}{\gamma}$. With these expressions it is possible to fit the experimentally constructed correlation functions very well, using the interfacial tension and the capillary length or the capillary time as fit parameters.[1]

However, recent experiments have shown that for the capillary waves in aqueous PMMA-Xanthan mixtures there is a discrepancy between the interfacial tension obtained from the static and dynamic correlation functions. The value obtained from the dynamic correlation function is consistently higher than the one from the static correlation function (factor of ~ 1.75).[2,3] Therefore, the aim of this work is to find out the reason behind this discrepancy.

Firstly, we considered the influence of the rheological properties of the fluid phases on the interface dynamics. Especially the colloidal gas phase exhibits strong shear thinning behaviour, which we tried to incorporate by using a decay rate dependent viscosity in the derivation of the dynamic correlation function.

Another point we will discuss is the fact that both colloid and polymer are relatively large (with a hydrodynamic radius $R_h = 112$ nm and a radius of gyration $R_g = 222$ nm respectively) and therefore also relatively slowly diffusing. We took this into account by adding a diffusion term ($\mathrm{D}q^2$) to the decay of each wave mode.

Finally, we investigated whether the equilibration time that is needed to reach the mean-field depletion attraction force[4] could possibly interfere with the interface dynamics. This equilibration time strongly depends on the colloid-polymer size ratio, so we studied the capillary waves in mixtures with twice as large PMMA particles.

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