Supporting Information

Model-independent analysis of QCM data on colloidal particle adsorption.

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The central result of our study is the demonstration, that effects of object size (d, Figure 1 in the main text) and of surface coverage (θ, Figure 1 in the main text) on the QCM response for a heterogeneous film formed in liquid by adsorption can be separated by analysing the behaviour of the ratio of the bandwidth shift to the frequency shift: this ratio decreases with surface coverage but increases with the size of the adsorbing particles (Figure 3 in the main text). Here we show, that this ratio exhibits a different behaviour in the case a polymer gel formed in situ at the surface of the QCM crystal.

A gel of Poly-N-isopropyl acrylamide (polyNIPAM) is prepared *in situ* on gold-coated QCM crystals by electrochemically induced free radical polymerisation. Experimental details are presented in Reuber et al.[1] Here, we show a representative plot of frequency and bandwidth shifts as a function of polymerisation time (Figure S1a), and the plot of the bandwidth shift to frequency shift ratio as a function of the frequency shift (Figure S1b). After an initial sharp decrease, the ratio increases, as the thickness of the polymer film increases. This behaviour is clearly different form that observed with colloidal particles (Figure 3 in the main text).

The initial sharp drop in the ratio is due to a combination of two factors. Firstly, at the initial stages of polymerisation, the magnitudes of the frequency and bandwidth shifts are quite small indeed, and the $\Delta\Gamma/-\Delta F$ ratio is obtained by dividing two very small numbers by each other. It is therefore not clear, to which extent the initial sharp decrease of the ratio is real. Secondly, at the initial stages, the polymer film is unlikely to be homogeneous. Hydrodynamic effects, at work in the case of colloidal particle adsorption, will operate in this situation as well.
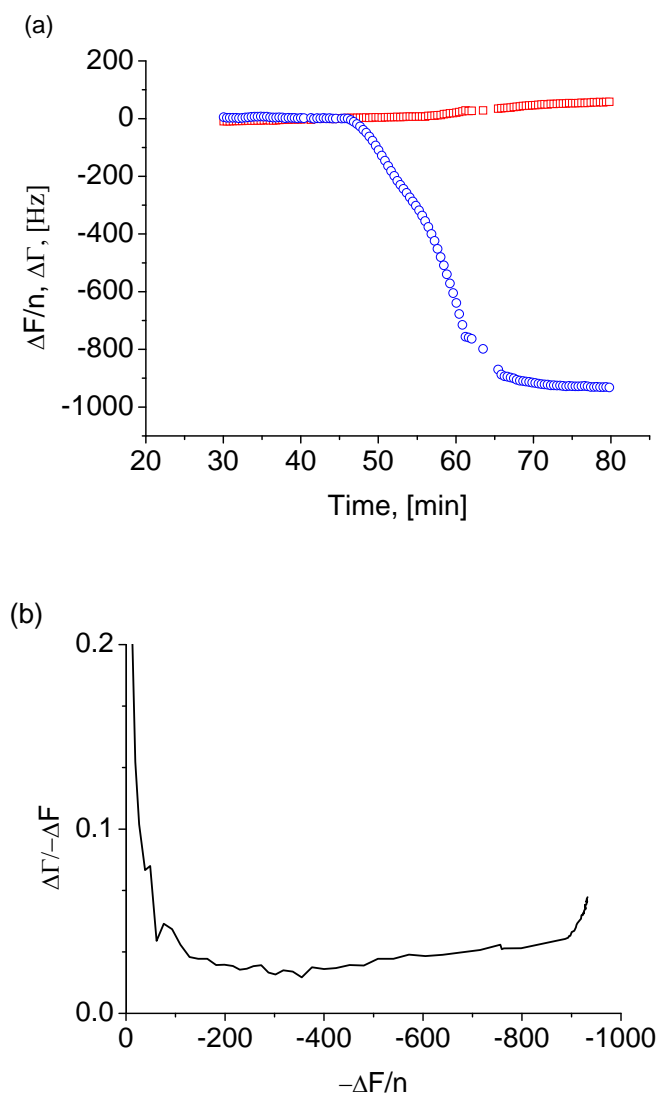
(a)

(b)

Figure S1: Formation of a pNIPAM gel on a gold-coated QCM crystal by electrochemically induced free radical polymerisation.

(a) The frequency shift (blue circles) decreases, while the bandwidth (red squares) increases, as a function of polymerisation time.

(b) The ratio of the bandwidth shift to frequency shifts exhibits a complex behaviour, with an initial sharp decrease (up to ~ 20% of the final asymptotic frequency shift), followed by a slow increase, and finally a sharp rise. This behaviour is clearly different from that

observed in the case of adsorbing colloidal particles described in the main text of the manuscript.

1.   Reuber, J.; Reinhardt, H.; Johannsmann, D., *Langmuir* **2006,** *22*, (7), 3362-3367.