Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information - Using adsorption kinetics to assemble vertically aligned nanorods at liquid interfaces for metamaterial applications

S.O. Morgan[a], A. Muravitskaya[a], C. Lowe[a], A.M. Adawi[a], J.-S.G. Bouillard[a], T.S. Horozov[b], G.J. Stasiuk[c], D.M.A. Buzza*[a]

[a]*Department of Physics & Mathematics, University of Hull, Hull HU6 7RX, U.K.*
[b]*Department of Chemistry & Biochemistry, University of Hull, Hull HU6 7RX, U.K.*
[c]*Imaging Chemistry & Biology, King's College London, Strand, London WC2R 2LS, U.K.*

Adsorption kinetics of neutrally wetting cylinders at a bare liquid interface

In Figure S1, we present the adsorption trajectories for neutrally wetting cylinders ($\theta_w = 90°$) with different aspect ratios calculated using different assumptions. Specifically, the top, middle and bottom row show results for aspect ratios $m = 1, 2.5$ and 5 respectively. On the other hand, the left, middle and right columns show the results for model 1 (flat interface + Scaling 1), model 2 (flat interface + Scaling 2) and model 3 (deformed interface + Scaling 2) respectively (see Section2 for details of these models).

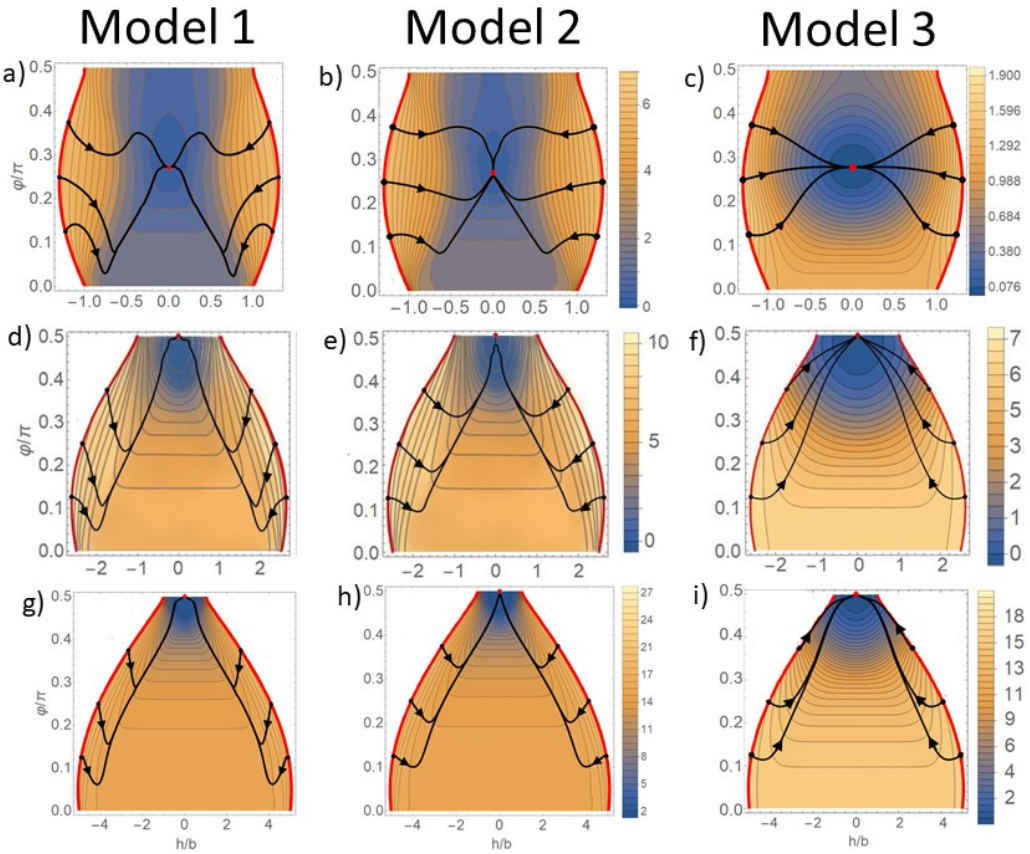

Figure S1 Adsorption trajectories of cylindrical nanorods with $\theta_w = 90°$, $\eta = 20$ for aspect ratio $m = 1$ (top row), $m = 2.5$ (middle row), $m = 5$ (bottom row) calculated from model 1 (left column), model 2 (middle column) and model 3 (right column). The solid red curves are the height of the cylinder when it first contacts the liquid interface as a function of particle orientation $h_c(\phi)$, the red dots are the stable states of the nanorod and the solid black curves are the adsorption trajectories. The trajectories are superposed on contour plots of the free energy landscape.

Note that as discussed in Section 3.1 and Figure 2 of the main paper, there is only one stable orientation for neutrally wetting cylinders. Specifically, for $m = 2.5$ and 5, the equilibrium state is the side-on state $\phi = \pm 90°$ while for $m = 1$, the equilibrium state is the tilted state, with a tilt angle $\phi = \pm 49.6°$ for the deformed interface model. These stable states are represented by the red dots in Figure S1. Since there is only one stable state in this case, the phase plan diagram for neutrally wetting cylinders do not possess a separatrix.

We next consider the impact of the calculational model used on the adsorption process of cylinders. For all the aspect ratios shown in Figure S1, we see that for model 1, there is generally strong non-monotonic variation of the particle orientation ϕ along the adsorption trajectory, with ϕ initially moving away from the stable state orientation before moving towards the stable state value at the later stages of the adsorption. However, as we go to model 2 then to model 3, the non-monotonic variation of ϕ is either strongly reduced or disappears altogether. This trend is similar to what we saw in Figure 4 of the main paper for non-neutrally wetting cylinders.

Finally, we note that for neutrally wetting cylinders with $m = 2.5, 5$, the adsorption trajectories of particles approaching the liquid interface from the oil side do not converge onto the same dynamical attractors as particles approaching from the water side. Indeed, dynamical attractors are absent altogether for neutrally wetting cylinders with $m = 1$. These results are in contrast to what we found for non-neutrally wetting cylinders (Figure 4 in main paper) where dynamical attractors are present for all the aspect ratios studied and the adsorption trajectories of particles approaching the interface from either the oil side or the water side converge onto the same dynamical attractors. Note that the absence of dynamical attractors for neutrally wetting particles is consistent with what we observed for the adsorption of ellipsoids at liquid interfaces in ref.[1].

Range of Dispersion Forces for GNRs at Oil/Water Interface

In this section, we estimate the range of dispersion forces for Gold Nanorods (GNRs) adsorbed at or approaching an oil/water interface.

For vertical hydrophilic nanorods with length $L = 2a$, radius b which are attached to the oil/water interface and primarily immersed in the water phase, the dispersion interaction energy between two nanorods with surface-to-surface separation d through the water phase is given by [2]

$$U(d) = -\frac{A_{AuWAu} L b^{1/2}}{24 d^{3/2}} \qquad [1]$$

where A_{AuWAu} is the Hamaker constant for gold interacting with gold through water. By setting the interaction energy in Eq.(1) to the thermal energy kT and rearranging, we find that the critical distance between two GNRs below which dispersion forces become significant is

$$d_{c1} = \left(\frac{A_{AuWAu} L b^{1/2}}{24 kT}\right)^{2/3}. \qquad [2]$$

For $L = 120$ nm, $b = 25$ nm and $A_{AuWAu} = 4 \times 10^{-20}$ J [2] we find $d_{c1} \approx 200$ nm.

For a hydrophilic GNR approaching the oil/water interface from the water side, if we approximate the nanorod tip closest to the interface as a sphere of radius b, the dispersion interaction energy between the nanorod and the oil phase with surface-to-surface separation d is [2]

$$U(d) = -\frac{A_{AuWO} b}{6d} \qquad [3]$$

where A_{AuWO} is the Hamaker constant for gold interacting with oil through water which can be calculated from $A_{AuWO} = \sqrt{A_{AuWAu}A_{OWO}}$ where A_{OWO} is the Hamaker constant for oil interacting with oil through water [2]. Setting the interaction energy in Eq.(3) to the thermal energy, we find the critical distance between the GNR and the interface below which dispersion forces become important to be

$$d_{c2} = \frac{A_{AuWO}b}{6kT}. \qquad [4]$$

For $A_{OWO} = 0.5 \times 10^{-20}$ J [2] and $b = 25$ nm we find $d_{c2} \approx 40$ nm.

References

1. S. O. Morgan, J. Fox, C. Lowe, A. M. Adawi, J.-S. G. Bouillard, G. J. Stasiuk, T. S. Horozov, and D. M. A. Buzza, *Phys. Rev. E*, 2021, **103**, 042604.
2. J. Israelachvilli, *Intermolecular & Surface Forces*, 2nd Ed., Academic Press, 1991.