Chains of Cubic Colloids at Fluid-Fluid Interfaces

SUPPLEMENTARY INFORMATION

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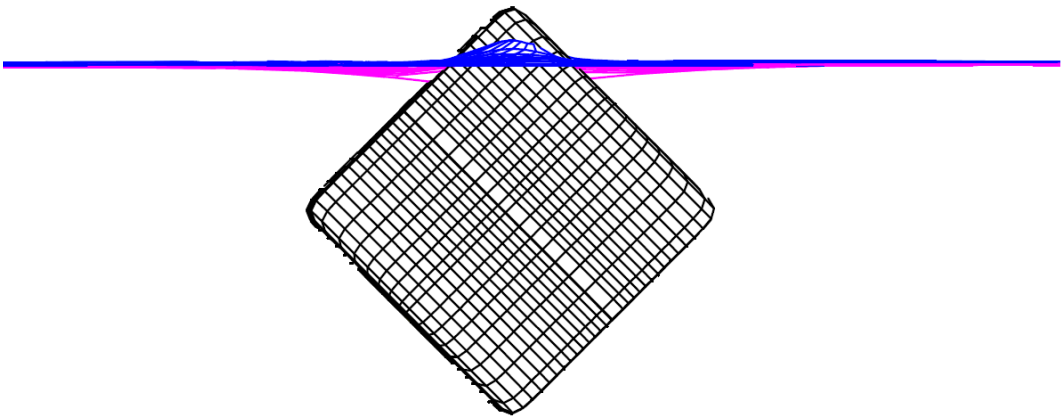

FIG. S1: Quadrupolar deformation field induced by a cubic particle with a Young contact angle $\cos\theta = 0.6$, adsorbed at a fluid-fluid interface in the "edge up" {110} configuration.

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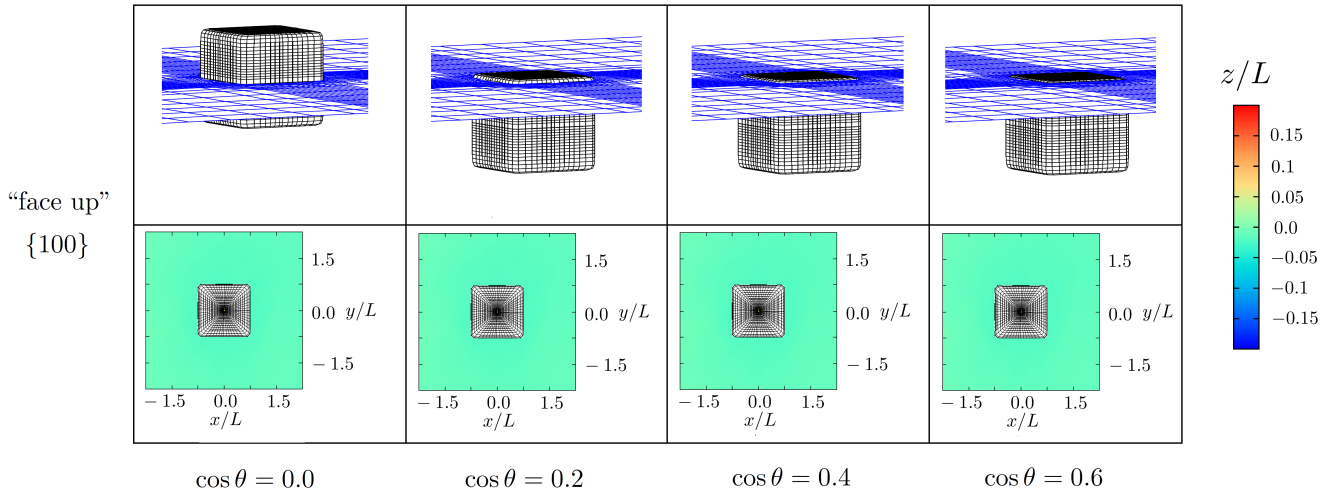

FIG. S2: Deformation field induced by a single cube of side L adsorbed at a fluid-fluid interface in the "face up" {100} configuration, for several Young contact angles θ. The particle in this configuration never deforms the interface.

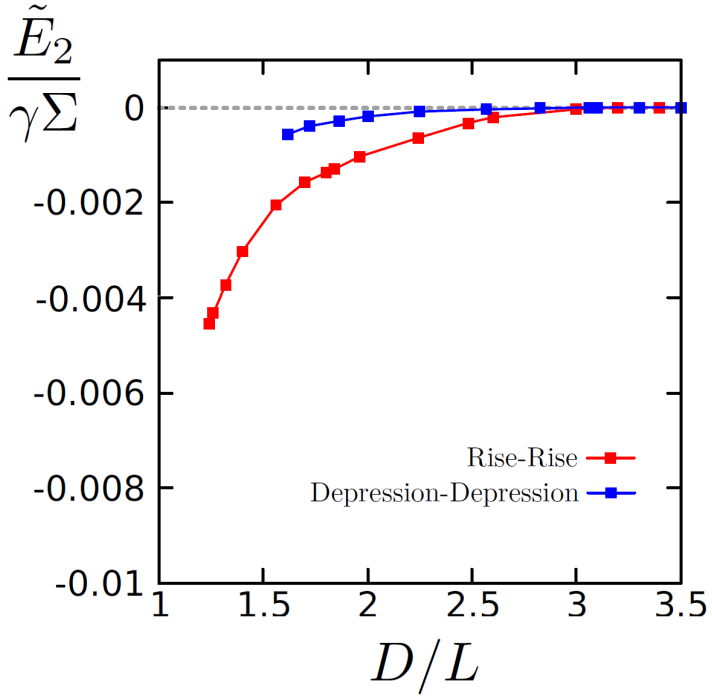

FIG. S3: Interaction energy per particle $\tilde{E}_2 \equiv E_2/2 - E_1$ of two cubes with side L and a Young contact angle $\cos\theta = 0.2$ adsorbed in the {110} configuration, as a function of the distance D between their centers of mass. In red the case of cubes with two overlapping rises is depicted, in blue the case of cubes with two overlapping depressions. The energy $\tilde{E}_2$ is plotted in units of $\gamma\Sigma$, with γ the fluid-fluid surface tension and Σ the surface area of the particle. E_1 and E_2 are given by Eq. 1 of the main paper, in the case $N = 1$ and $N = 2$, respectively.

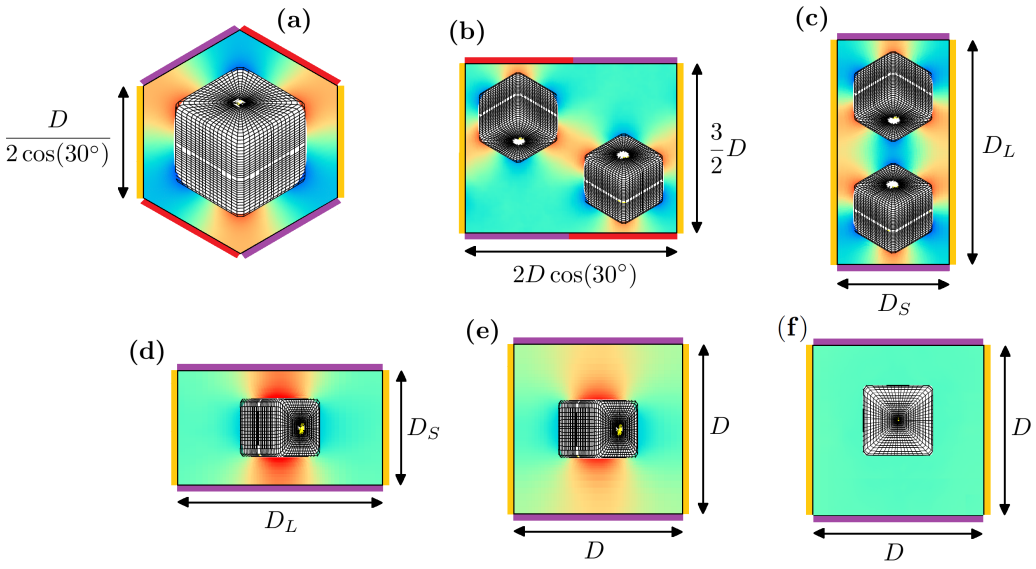

FIG. S4: We discuss here the lattice unit cells and the periodic boundary conditions (PBCs) used to define the several phases studied in section III of the main paper. Each unit cell is centered in $(x = 0, y = 0)$, and segments represented with the same colour have the same fluid-fluid interface height profile. **(a)** For the *hexagonal* phase x, we use a hexagonal unit cell with sides $D/(2\cos(30°))$, where D is the center-of-mass distance between two nearest-neighbor particles in the lattice. We apply the following PBCs to the cell sides: opposite sides of the hexagonal cell have the same fluid-fluid interface height profile. In the cell there is $N = 1$ particle in the $\{111\}$ configuration, and with (x_1, y_1, α_1) given by $(0, 0, 0)$. **(b)** For the *honeycomb* phase h, we use a rectangular cell with sides $2D\cos(30°)$ and $3D/2$, respectively, where D is the center-of-mass distance between two nearest-neighbor particles in the lattice. We apply the following PBCs to the cell sides: the half-side from $(-D\cos(30°), -3D/4)$ to $(0, -3D/4)$ has the same fluid-fluid interface height profile of the half-side from $(0, 3D/4)$ to $(D\cos(30°), 3D/4)$, the half-side from $(0, -3D/4)$ to $(D\cos(30°), -3D/4)$ has the same fluid-fluid interface height profile of the half-side from $(-D\cos(30°), 3D/4)$ to $(0, 3D/4)$, and the two remaining opposite sides of the cell have the same fluid-fluid interface height profile. In the cell there are $N = 2$ particles in the $\{111\}$ configuration, and with (x_i, y_i, α_i), for $i = 1, 2$, given by $(-D\cos(30°)/2, 3D/4, 0)$ and $(D\cos(30°)/2, -3D/4, \pi)$. **(c)** For the *"vertex up" square* phase $s_{\rm v}$, we consider a rectangular unit cell with sides D_S and D_L, respectively, where D_S and D_L are the center-of-mass distances between two nearest neighbor particles in the dipole-dipole bond direction of the lattice and in the tripole-tripole bond direction of the lattice, respectively. We apply the following PBCs to the cell sides: opposite sides of the square cell have the same fluid-fluid interface height profile. In the cell there are $N = 2$ particles in the $\{111\}$ configuration, and with (x_i, y_i, α_i) for $i = 1, 2$, given by $(0, -D_L/2, 0)$ and $(0, D_L/2, \pi)$. **(d)** For the *chains* phase c, we use a rectangular unit cell with sides D_S and D_L, respectively, where D_S is the center-of-mass distance between two nearest-neighbor particles of the lattice. We instead choose $D_L \equiv D_L^* = 3.0L$, with L the side length of the cubic particles. D_L^* corresponds to the smallest distance for which two cubes in the $\{110\}$ configurations do not interact. In this way we describe the c phase as a "gas" of chains that do not interact laterally. We apply the following PBCs to the cell sides: opposite sides of the cell have the same fluid-fluid interface height profile. In the cell there is $N = 1$ particle in the $\{110\}$ configuration, and with (x_1, y_1, α_1) given by $(0, 0, 0)$. **(e)** For the *"edge up" square* phase $s_{\rm e}$, we use a square unit cell with side D, where D is the center-of-mass distance between two nearest-neighbor particles of the lattice. We apply the following PBCs to the cell sides: opposite sides of the cell have the same fluid-fluid interface height profile. In the cell there is $N = 1$ particle in the $\{110\}$ configuration, and with (x_1, y_1, α_1) given by $(0, 0, 0)$. **(f)** For the *"face up" square* phase $s_{\rm f}$, we use a square unit cell with sides D, where D is the center-of-mass distance between two nearest-neighbor particles of the lattice. We apply the following PBCs to the cell sides: opposite sides of the cell have the same fluid-fluid interface height profile. In the cell there is $N = 1$ particle in the $\{100\}$ configuration, and with (x_1, y_1, α_1) given by $(0, 0, 0)$.
By tuning D for the phases x, h, $s_{\rm e}$, and $s_{\rm f}$, and D_S, D_L for the phases $s_{\rm v}$ and c, we regulate the lattice spacing, and therefore the particle packing fraction η in the lattice. η is given by $\eta = 2/(\sqrt{3}D^2)$ for the phase x, by $\eta = 4/(3\sqrt{3}D^2)$ for the phase h, by $\eta = 1/(D_S D_L)$ for the phases $s_{\rm v}$ and c, and by $\eta = 1/(D^2)$ for the phases $s_{\rm e}$ and $s_{\rm f}$.

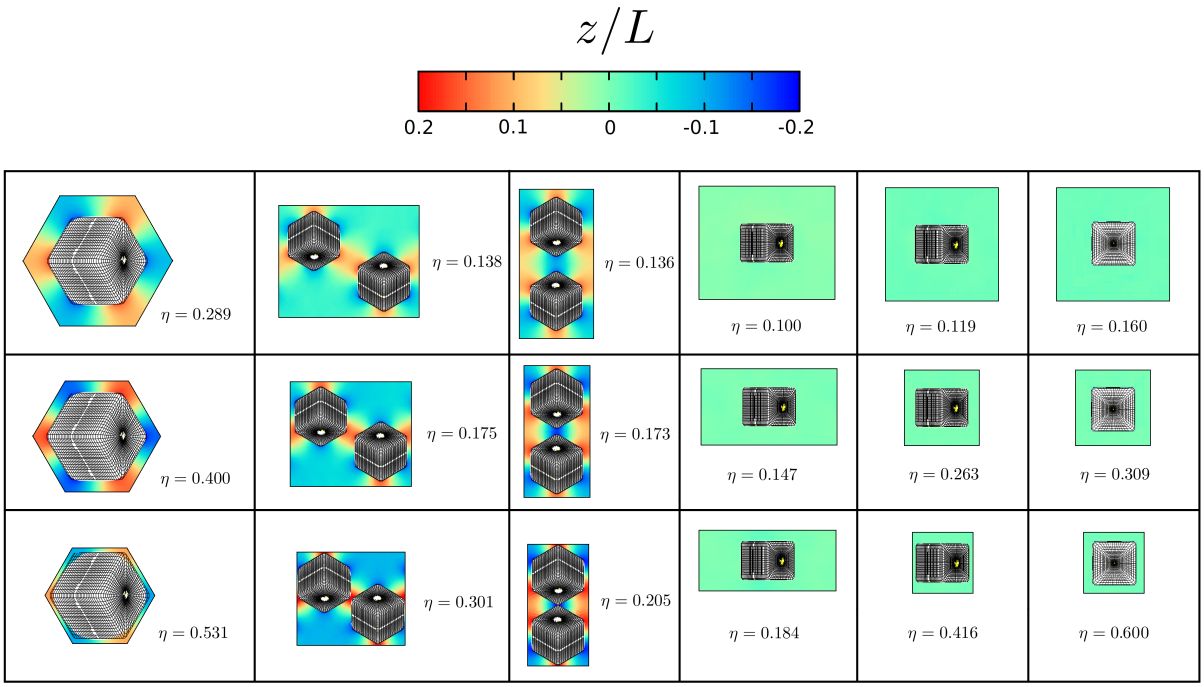

FIG. S5: Contour plot of the fluid-fluid interface height profile, as obtained by our numerical method, in a unit cell of phase x, h, s_{v}, c, s_{e} and s_{f} (from left to right, respectively) at a fixed Young contact angle $\cos\theta = 0.0$. Note that PBCs are applied to the lattice unit cells, as described in Fig. S4. Each lattice unit cell is shown for a given packing fraction η. The plane $z = 0$ corresponds to the fluid-fluid interface when no particle is adsorbed. With L we denote the side of the cube.

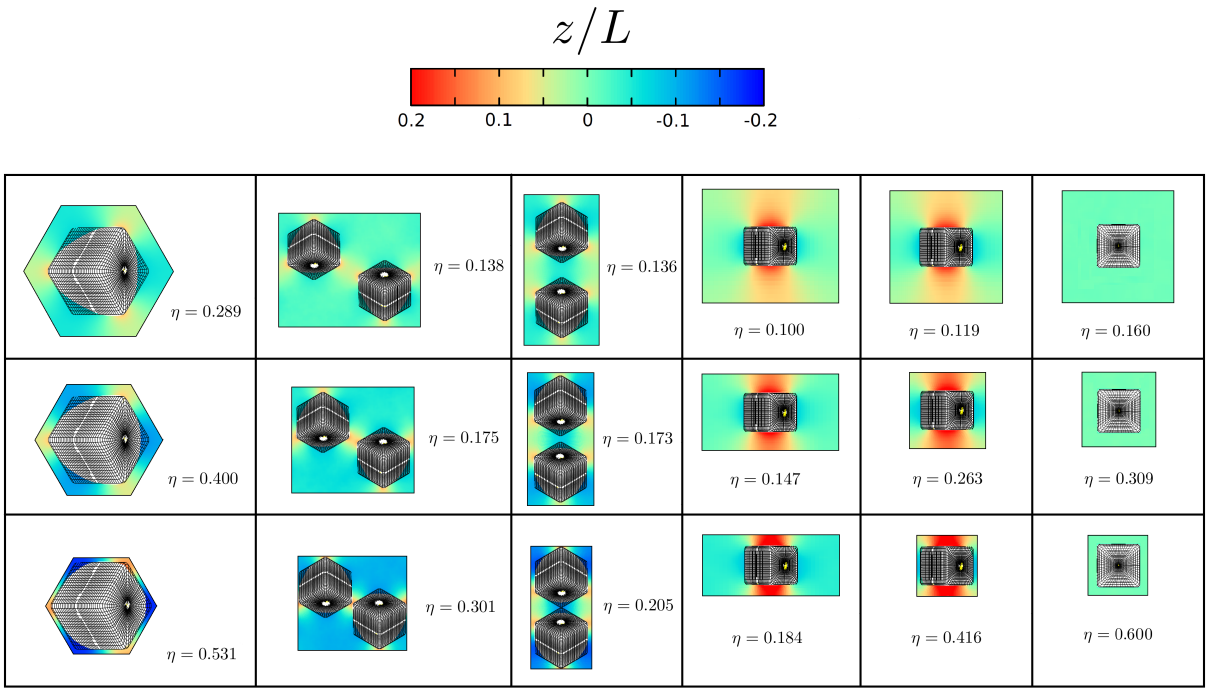

FIG. S6: Contour plot of the fluid-fluid interface height profile, as obtained by our numerical method, in a unit cell of phase x, h, s_{v}, c, s_{e} and s_{f} (from left to right, respectively) at a fixed Young contact angle $\cos\theta = 0.4$. Note that PBCs are applied to the lattice unit cells, as described in Fig. S4. Each lattice unit cell is shown for a given packing fraction η. The plane $z = 0$ corresponds to the fluid-fluid interface when no particle is adsorbed. With L we denote the side of the cube.

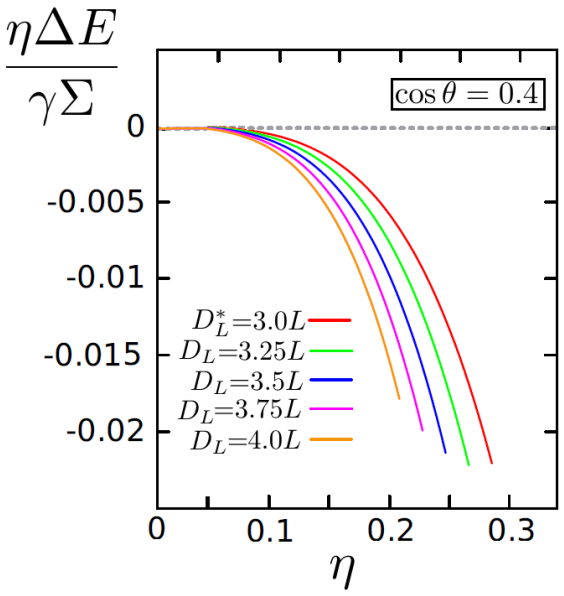

FIG. S7: Dimensionless (capillary) interaction energy per unit area $\eta\Delta E/(\gamma\Sigma)$ in the c phase as a function of the particle packing fraction η, for $\cos\theta = 0.4$. $\Delta E \equiv E_N/N - E_1^{\{110\}}$ is the (capillary) interaction energy per particle minus the adsorption energy of a single particle in the $\{110\}$ configuration, and is expressed in units of $\gamma\Sigma$, where γ is the fluid-fluid surface tension and Σ is the surface area of a particle. With the different colours we indicate $\eta\Delta E/(\gamma\Sigma)$ computed for several values of the lateral distance D_L among the chains (see Fig. S4 and the main manuscript). $D_L^* = 3L$ (with L denoting the side of the cube) corresponds to the smallest distance for which two cubes in the $\{110\}$ configurations do not interact. We observe that considering $D_L > D_L^*$ does not significantly affect the η dependence of $\eta\Delta E$, unless D_L is too large.

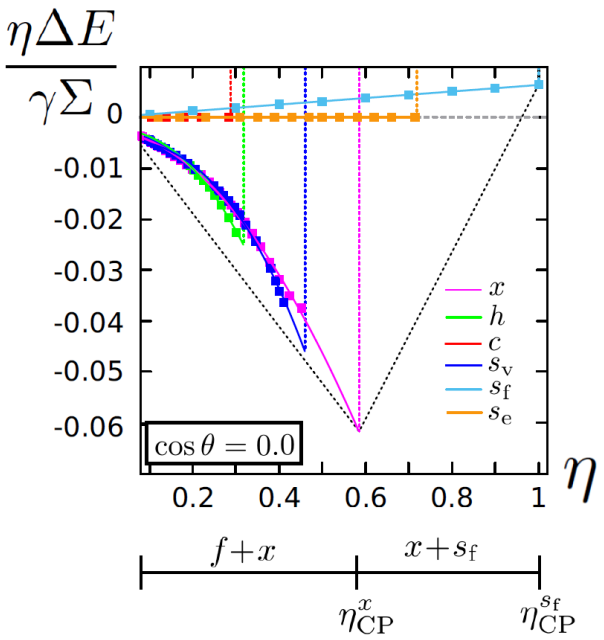

FIG. S8: Dimensionless (capillary) interaction energy per unit area $\eta\Delta E/(\gamma\Sigma)$ as a function of the particle packing fraction η, for $\cos\theta = 0.0$. $\eta^{\xi}_{\rm CP}$ indicates the closest-packing of $\xi = x, s_{\rm f}$. $\Delta E \equiv E_N/N - E_1^{\{110\}}$ is the (capillary) interaction energy per particle minus the adsorption energy of a single particle in the $\{110\}$ configuration, and is expressed in units of $\gamma\Sigma$, where γ is the fluid-fluid surface tension and Σ is the surface area of a particle. We show results for the phase with chains c (*red*), the hexagonal phase x (*magenta*), the "face up" square phase $s_{\rm f}$ (*light-blue*), the "edge up" square phase $s_{\rm e}$ (*yellow*), the "vertex up" square phase $s_{\rm v}$ (*blue*), and the honeycomb phase h (*green*). Dotted black lines indicate the common tangent construction. We see that an extremely dilute disordered fluid phase f coexists with the close-packed x phase for $\eta < \eta^{x}_{\rm CP}$, while for $\eta > \eta^{x}_{\rm CP}$ the close-packed x phase coexists with the close-packed $s_{\rm f}$ phase.