

Supplementary Material to “Controlled Deposition of Nanoparticles with Critical Casimir Forces”

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S1. EXPERIMENTAL DETAILS

A. QD synthesis

We have synthesized cadmium selenide (CdSe) quantum dots (QDs) of diameter $d_{QD} = 5.5$ nm (polydispersity 13%) by following the reported procedure [1].

B. QD ligand exchange with DMPS ligands

The native hydrophobic oleate ligands were replaced with hydrophilic 2,3-dimercapto-1-propanesulfonates (DMPS) by using a two-phase system where a $40\mu\text{M}$ dispersion of QDs in hexane was placed in contact with a 40 mM solution of DMPS in N-methylformamide. After stirring the mixture vigorously for 1 hour, the QDs migrated to the polar phase as a consequence of the ligand exchange. The polar phase was collected and QDs were precipitated by adding an additional volume of acetonitrile. After centrifugation at 3000 g for 20 min, the clear supernatant was discarded and QDs were redispersed at a concentration of $2\mu\text{M}$ in the binary solvent, a 30w/w% solution of 2,6-lutidine in water, with an additional 10 mM NaOH to improve the colloidal stability of QDs.

C. Substrate surface treatment

A silicon substrate was made hydrophilic through 1 minute of plasma cleaning, or hydrophobic through a silanization treatment with 3-mercaptopropyl trimethoxysilane by following the literature (ref.[2], cleaning method 2, and stored under vacuum overnight prior to use). The silanization treatment resulted in a contact angle with water of 74° , see Fig. S1.

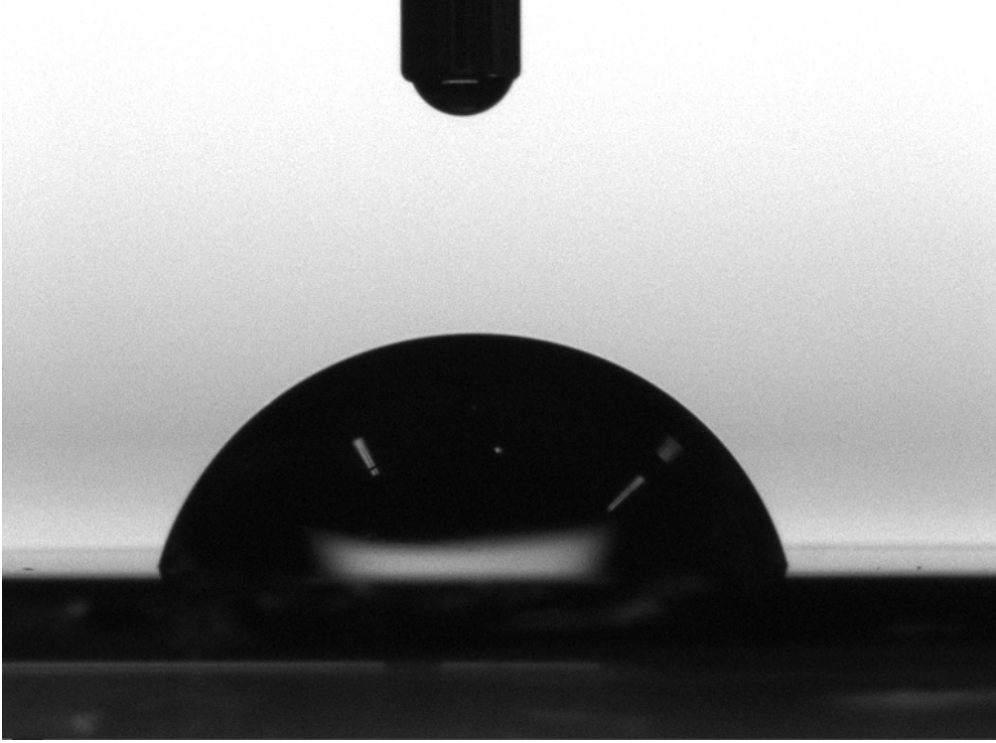


FIG. S1. **Contact angle measurement.** Contact angle measurement of the silanized silicon substrate with water. The measured contact angle is $74.4 \pm 0.4^\circ$.

D. QD epitaxial deposition using critical Casimir forces

A volume of 1.5 mL of the QD dispersion was added to a glass test tube (14 mm ID). The silicon substrate was placed in thermal contact with a cylindrical steel block (13.5 mm in diameter) and immersed in the binary solvent. The substrate was heated by means of a heating element embedded in the steel block and placed 0.3 mm from the surface, to temperature T , such that $\Delta T = T_s - T > 0$, where T_s is the phase separation temperature of the binary solvent. By keeping the bulk of the solvent at room temperature (RT), we established a vertical temperature gradient going from T in the proximity of the substrate to RT far from the substrate (Fig. 1a in the main text and Fig. S2). The magnitude of the critical Casimir interaction is strongly dependent on ΔT , since the size of the fluctuations follows a power-law dependence of the type $\xi \sim \xi_0 |\Delta T/T_s|^{-0.63}$. This makes the surface of the substrate the only active location for QD deposition. To ensure maximum reproducibility, we measured the size of the solvent density fluctuations prior to each deposition in proximity

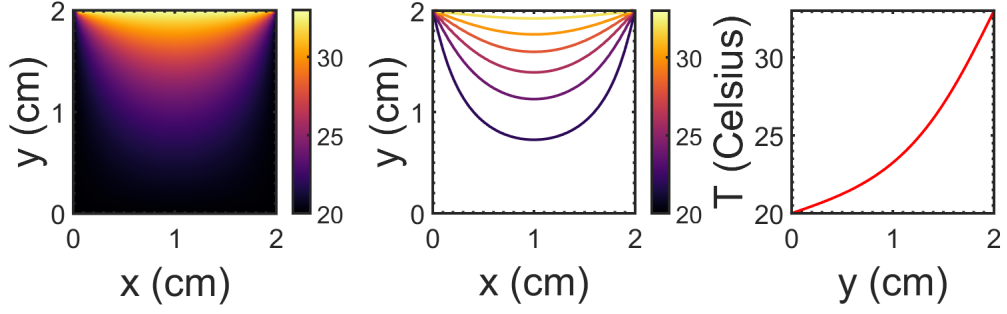


FIG. S2. **Calculated temperature distribution in the binary solvent.** Calculated temperature distribution in the binary solvent considering heating from the top ($T(y = 2 \text{ cm}) = 33^\circ\text{C}$) while the other walls of the container are in good thermal contact with a room-temperature bath ($T(x = 0) = T(x = 2) = T(y = 0) = 20^\circ\text{C}$). The temperature range used for the assembly was 20°C to 33°C .

of the substrate with dynamic light scattering by measuring the hydrodynamic diameter of the fluctuations and correcting for the ΔT -dependence of the viscosity [3]. All micrographs shown in the main text correspond to a deposition time of one hour. Longer deposition times lead to an increase in the amount of deposited material, as shown in Fig. S3. After each deposition, the silicon substrate was retrieved, dipped in acetonitrile, and dried under vacuum prior to imaging.

E. Scanning electron microscopy

Electron micrographs were collected by using a Verios XHR SEM microscope (FEI) operated at 5 kV and 100 pA .

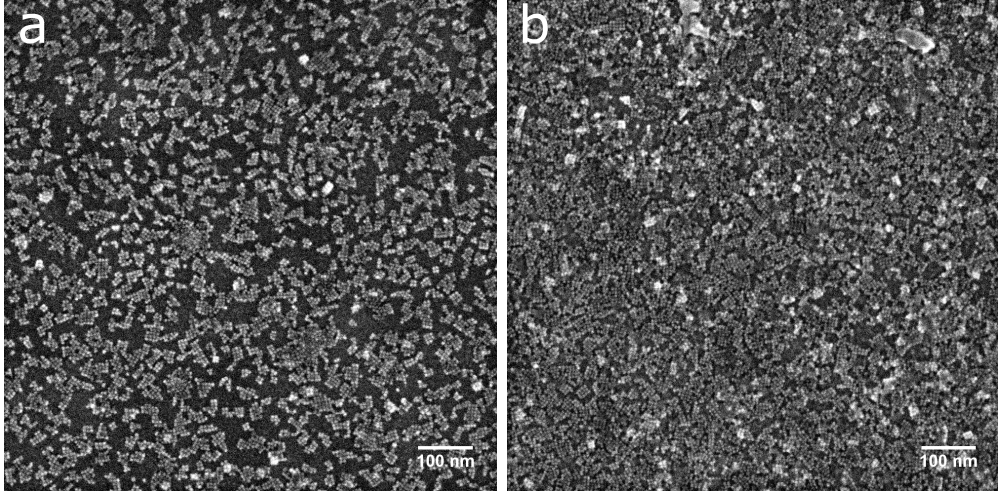


FIG. S3. **Effect of longer deposition times.** Scanning electron micrographs of hydrophilic silicon substrates retrieved from the QD deposition mixture after (a) 1 hour and (b) 3 hours of deposition for the correlation length $\xi = 6$ nm and the Debye length $\lambda_D = 15$ nm.

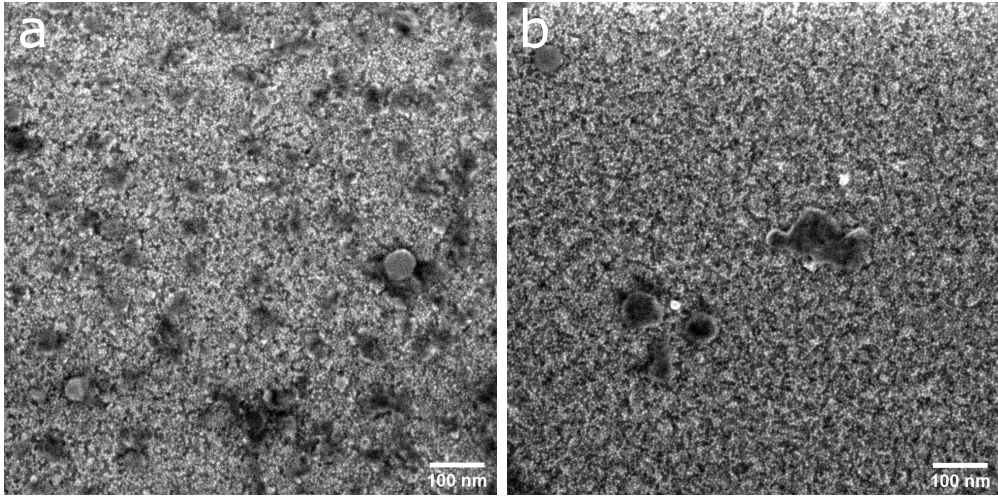


FIG. S4. **QD deposition on a gold substrate.** Scanning electron micrographs of gold (SiO2/Ti/Au prepared by sputtering) substrates retrieved from the QD deposition mixture after 1 hour of deposition for the correlation length $\xi = 6$ nm and the Debye length (a) $\lambda_D = 10$ nm and (b) $\lambda_D = 25$ nm.

S2. ELECTROSTATIC INTERACTIONS

A. QD-QD

In our energy minimization and MD simulations (Section S4 A and S4 B), we used the DLVO theory [4] to describe the electrostatic repulsion between quantum dots

$$\beta U_{\text{el}}(r) = \frac{Z^2 \lambda_B}{(1 + d_{QD}/2\lambda_D)^2} \frac{e^{-(r-d_{QD})/\lambda_D}}{r}, \quad (\text{S1})$$

where r is the center-to-center distance between two QDs, Z is the charge (in units of the elementary charge e), $\lambda_B = \beta e^2 / (4\pi\epsilon_r\epsilon)$ is the Bjerrum length and $\lambda_D = (8\pi\rho l_B)^{-1/2}$ the Debye screening length (all in Gaussian units). Here ρ is the salt concentration, ϵ the vacuum permittivity and ϵ_r the relative dielectric constant.

In all calculations, we took $\epsilon_r = 7$ corresponding to a critical water-lutidine mixture [5], which gives $\lambda_B \approx 8$ nm at room temperature. We used the renormalized colloidal charge [6] $Z = 2.13$ ($Z = 0.2Z_{\text{bare}}$ with $Z_{\text{bare}} = 7.1$ in water as estimated from ζ potential).

B. QD-substrate

Electrostatic interaction potential between a QD and a substrate is [4]

$$\beta U_{\text{el}}(D) = A_{\text{el}} e^{-D/\lambda_D}, \quad (\text{S2})$$

where D is the surface-to-surface distance between the QD and the substrate. The amplitude A_{el} is [4]

$$A_{\text{el}} = \frac{8d_{QD}}{\lambda_B} \tanh\left(\frac{e\psi_{QD}}{4k_B T}\right) \tanh\left(\frac{e\psi_s}{4k_B T}\right), \quad (\text{S3})$$

where ψ_{QD} and ψ_s are the surface potentials of the quantum dot and the substrate. Surface potentials are related to surface charge densities σ_α ($\alpha = \{QD, s\}$) by the Grahame equation

$$\sigma_\alpha = \sqrt{8\epsilon_0\epsilon_r k_B T \rho} \sinh\left(\frac{e\psi_\alpha}{2k_B T}\right). \quad (\text{S4})$$

For surface potentials below the thermal voltage, $\psi_\alpha \ll 2k_B T/e$, eq. S4 gives

$$\sigma_\alpha \approx \epsilon_0\epsilon_r \psi_\alpha / \lambda_D. \quad (\text{S5})$$

For low surface potentials, eq. S3 thus becomes

$$A_{\text{el}} = 8\pi^2 d_{QD} \lambda_D^2 \lambda_B \sigma_{QD} \sigma_s / e^2. \quad (\text{S6})$$

Thus, the strength of the electrostatic repulsion increases rapidly with increasing λ_D . Figure 1b,c (main text) shows that for a fixed correlation length ($\xi = 5 \text{ nm}$), the effect of λ_D on the surface coverage is moderate, implying rather weak electrostatic repulsion and low surface charge densities.

To demonstrate the effect of the Debye screening length on the total interaction potential, we used the following parameters to produce Fig. 3c of the main text: Bjerrum length $\lambda_B = 8 \text{ nm}$ (corresponding to $\varepsilon_r = 7$ of water-lutidine [5]), QD diameter $d_{QD} = 5.5 \text{ nm}$ and the product of the surface charge densities $\sigma_{QD} \sigma_s = 1.5 \times 10^{-6} \text{ e}^2/\text{nm}^4$.

S3. CRITICAL CASIMIR INTERACTIONS

We have used Monte Carlo simulations of the Ising model to calculate critical Casimir interactions between a quantum dot and a substrate and between two quantum dots at a substrate. The Ising model mimics an incompressible binary liquid mixture or a simple fluid. MC simulations of this model is a reliable and computationally feasible tool to compute critical Casimir potentials in the proximity of criticality.

A. Monte Carlo simulations

The Hamiltonian of the Ising model is given by

$$H(\{s\}) = -J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i, \quad (\text{S7})$$

where J is the coupling constant, $s_i = \pm 1$ is a classical spin at lattice site i , corresponding to the occupation of site i by one or another species of a binary liquid mixture, and h is the external ‘magnetic’ bulk field, corresponding to the difference in the chemical potentials of two species. The sum $\langle ij \rangle$ runs over all neighboring pairs of spins. The spins belonging to the interior of the QD and the substrate were frozen and set to the values dictated by the boundary conditions. We considered hydrophilic QDs and hydrophilic substrates (*i.e.*, the same values of the spin, say $s = -1$) as well as hydrophobic substrates ($s = +1$) with a hydrophilic patch ($s = -1$ within the patch). The summation in eq. S7 runs only over non-frozen lattice sites, corresponding to the space accessible to the binary mixture. The critical Casimir interaction potential was computed by using the local field approach [7, 8].

In all simulations, the system size was $L_x \times L_y \times L_z = 50 \times 50 \times 80$ lattice units in the x , y and z directions, respectively. Periodic boundary conditions were applied in the x and y directions; the spins were fixed at the bottom substrate ($z = 0$), as described above, and free boundary conditions were applied at the top surface at $z = L_z$ (*i.e.*, the spins on that surface were allowed to fluctuate). The QD diameter was 11 lattice sites. The averaging was performed over 5×10^6 hybrid Monte Carlo steps [9] with preliminary thermalization of 5×10^5 MC steps.

To extract the decay length λ_{Cas} ($\approx \xi$) of the critical Casimir potential U_{Cas} , we fitted

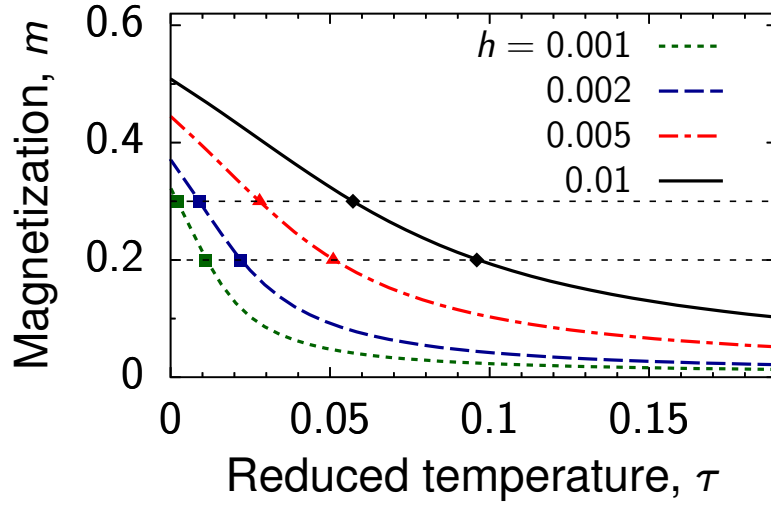


FIG. S5. **Magnetization m and constant m path.** Bulk magnetization as a function of the reduced temperature $\tau = (T - T_c)/T_c$, where T_c is the critical point, obtained by Monte Carlo simulations of the Ising model in bulk (no substrates or colloids). The horizontal dashed line shows the thermodynamic path taken to calculate the critical Casimir potentials. The corresponding points for the chosen magnetic fields are marked by symbols and read $(h, t) \approx (0.001, 0.002)$, $(0.002, 0.009)$, $(0.005, 0.028)$, and $(0.01, 0.057)$ for $m = 0.3$ and $(h, t) \approx (0.001, 0.011)$, $(0.002, 0.022)$, $(0.005, 0.051)$, and $(0.01, 0.096)$ for $m = 0.2$.

the MC data with the following function

$$U_{\text{Cas}}(D) = \frac{A_{\text{Cas}}}{D + a} e^{-D/\lambda_{\text{Cas}}}, \quad (\text{S8})$$

where D is the surface-to-surface distance, parameter a describes a non-universal behavior at short separations and A_{Cas} is a constant.

B. Thermodynamic path

In the experiments (Section S1), the molar fraction of water-lutidine was kept off-critical and the temperature was varied to approach the water-lutidine separation temperature. To mimic this thermodynamic path, we performed MC simulations and computed the critical Casimir potentials at a constant average magnetization $m = \langle s \rangle$. To this end, we first simulated a bulk system for various bulk magnetic fields and temperatures. The result is

shown in Fig. S5, which shows the magnetization as a function of the reduced temperature $\tau = (T - T_c)/T_c$ for a few values of the magnetic field h . The critical Casimir potentials were then computed for the values of the bulk magnetic field h and the reduced temperature τ that provide the bulk magnetization $m = 0.2$ (Fig. 2 in the main text) and $m = 0.3$ (Fig. 4 in the main text).

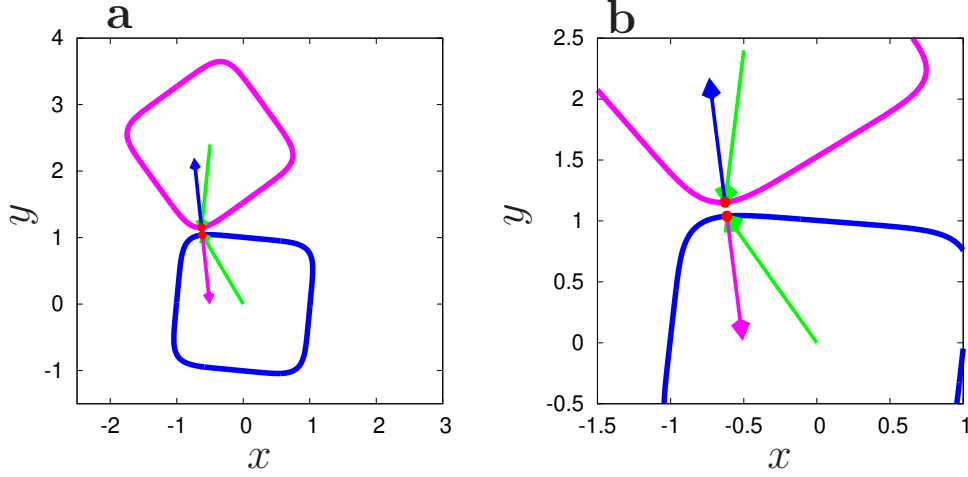


FIG. S6. **Two cubo-spherical particles on a substrate.** (a) Forces and torques acting between two cubo-spherical particles attached to a substrate. Green vectors are the directions to the two closest points of the surfaces; these points are denoted by red circles. (b) More detailed view of the near-contact area.

S4. ORDERING OF CUBO-SPHERICAL PARTICLES

To study how the shape of quantum dots affects the deposited structure, we have investigated ordering of cubo-spherical particles with the shape given by eq. 1 of the main text. Although this equation describes a three-dimensional object (see Fig. 1d of the main text), we studied ordering of such particles deposited on a substrate, with the particles' facets laying on the substrate. This is effectively a two-dimensional system of particles with the shape intermediate between a circle and a square. However, the electrostatic and critical Casimir forces acting between the particles were computed in three-dimensions, albeit for spherical particles inscribed into the corresponding cubo-sphere; the details of these interaction potentials are provided in Section S2 A and S3.

To take into account the particle shape, one can proceed as follows:

1. Identify two points of the closest approach on the two surfaces (red dots in Fig. S6) and radius-vectors to them from the centers of each particle (green vectors); the distance between these points is r_{12} .
2. Compute the repulsive force, which we chose to be

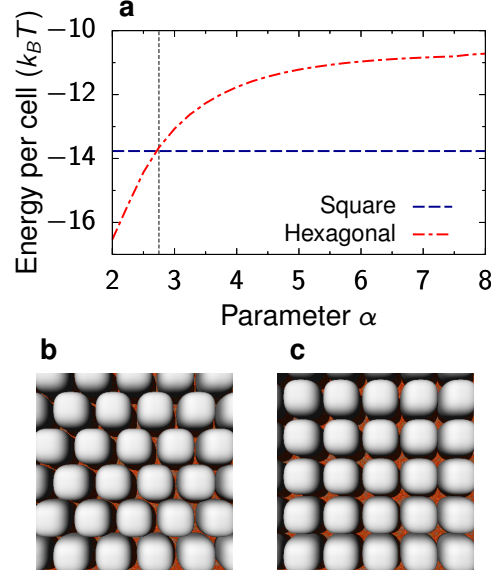


FIG. S7. **Optimal lattice of cubo-spherical particles deposited on a substrate.** (a) Energy per unit cell as a function of parameter α (eq. 1 of the main text) for a square and hexagonal lattice. Examples of (b) hexagonal and (c) square ordering for $\alpha = 2.75$ (vertical line in (a)).

$$U_{\text{rep}}(r_{12}) = \frac{A_{\text{rep}}}{r_{12}^7} \quad (\text{S9})$$

with $\beta A_{\text{rep}} = 1.78 \times 10^{-8}$ (as in ref. 10)

3. Repulsive forces act along the line $\mathbf{r}_{12}$ between these two closest point. Torques for these forces were computed with respect to the appropriate arms (green vectors in Fig. S6).

A. Energy minimization

We first computed the total energy for the system of cubo-spherical particles forming a square and a hexagonal lattice. We considered the separation between the particles as an optimization parameter but, for simplicity, we fixed the orientation of the particles such that the particles' facets face each other. Within this setup, the energy per unit cell, $\mathcal{E}$, for the square lattice does not depend on parameter α (eq. 1 of the main text). To find $\mathcal{E}$ for the hexagonal lattice, we wrote a computer program to minimize the energy over the cell size.

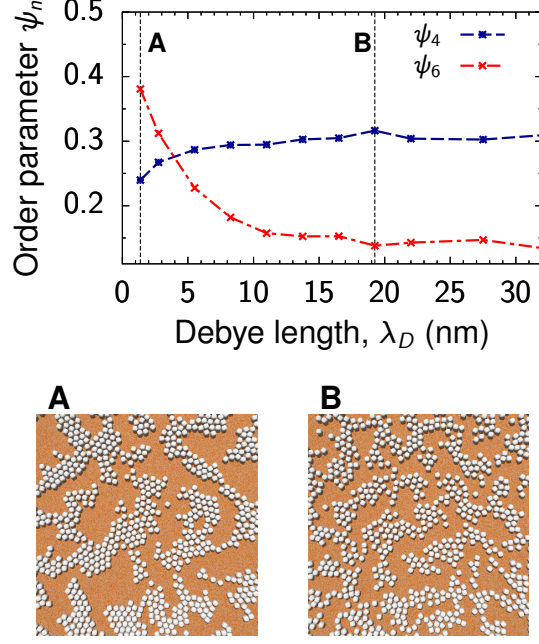


FIG. S8. **Transformation between hexagonal and quadratic ordering induced by the Debye screening length.** The top plot shows the square and hexatic order parameters (eq. S10) as functions of the Debye length, obtained by 2D molecular dynamics (MD) simulations, and the bottom plot shows two snapshots from the MD simulations. The critical Casimir potential between QDs was computed in the presence of a hydrophilic substrate for the reduced temperature $\tau = (T - T_c)/T_c = 0.007$ and bulk magnetic field of the Ising model $h = 0.01$. The electrostatic potential was calculated according to eq. S1. The critical Casimir and electrostatic interactions were computed for a spherical particle inscribed in the cubo-sphere with $\alpha = 3$ (eq. 1 of the main text).

We consider here a typical example: the Debye screening length $\lambda_D = 0.25d_{QD}$ and the critical Casimir potential computed for the reduced temperature $\tau = 0.007$ and bulk magnetic field $h = 0.01$ (see Section S2 A and S3). The results of the calculations are shown in Fig. S7, which demonstrates that the square lattice is energetically favourable for $\alpha > \alpha_0 \approx 2.71$.

B. Molecular dynamics simulations

We have also performed 2D molecular dynamics simulations of deposited cubo-spherical particles. We used our own computer program, as in ref. 10, but we had to include rotations because the particles are not spherically symmetric. For stability the rotational inertia (inertia with respect to rotations) had to be increased with respect to the moment of inertia of a sphere. The rotational friction coefficient was also increased. In these simulations we used the critical Casimir potential computed for the reduced temperature $\tau = 0.007$ and bulk magnetic field of the Ising model $h = 0.01$ in the presence of a hydrophilic substrate (Section S3). The critical Casimir and electrostatic potentials were calculated for a sphere inscribed in a cubo-spherical particle with given α .

C. Order parameters for 2D ordering

To quantify structures obtained from 2D molecular dynamics simulations, we computed the order parameters

$$\psi_k = \left\langle \sum_i^N \psi_k(i) \right\rangle, \quad (\text{S10})$$

where N is the total number of nanoparticles in a simulation box, $\langle \dots \rangle$ means thermal average and

$$\psi_k(i) = \frac{1}{n_i} \sum_{j=1}^{n_i} \cos(k\theta_{j,i,j+1}) \quad (\text{S11})$$

with n_i being the number of neighbors of the i th particle and $\theta_{j,i,j+1}$ the angle between particles i , j and $j+1$. We calculated ψ_4 ($= 1$ for a perfect square) and ψ_6 ($= 1$ for a perfect hexagonal lattice) within all clusters of nanoparticles; a particle was considered part of a cluster if the distance to at least one of the cluster's particles was smaller than 2.5 of the particle radius [10].

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