Supplementary Material for "Debye vs Casimir: controlling the structure of charged nanoparticles deposited on a substrate"

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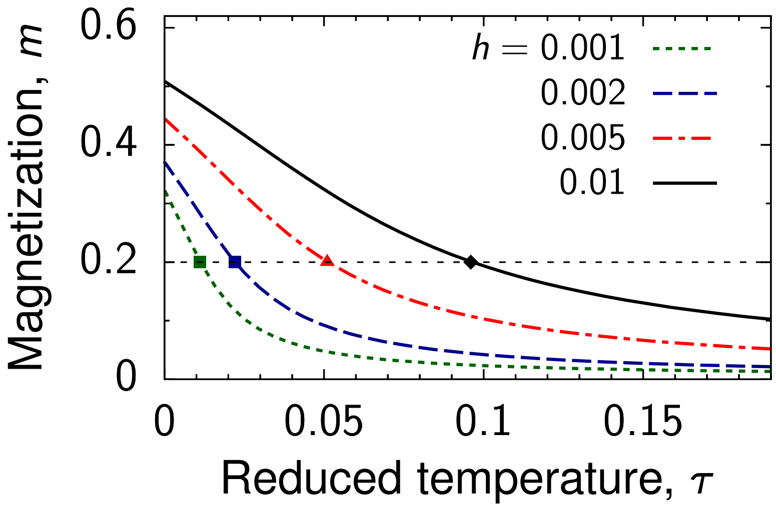

FIG. S1. **Path of constant magnetization.** Bulk magnetization as a function of reduced temperature $\tau = (T - T_c)/T_c$, where T_c is the critical point, obtained by Monte Carlo simulations of the Ising model in bulk (no substrates or colloids). The horizontal dashed line shows the thermodynamic path $m = 0.2$. For the values of the bulk field h and reduced temperature τ, see Table S1.

TABLE S1. **Path of constant magnetization.** Values of the bulk field h and reduced temperature τ providing the same bulk magnetization $m = 0.2$ in the Ising model.

h	τ	β
0.000200	0.000810701	0.221475
0.000220	0.00114973	0.221400
0.000240	0.00141207	0.221342
0.000260	0.00169265	0.22128
0.000300	0.00226789	0.221153
0.000400	0.00373387	0.22083
0.000600	0.00660559	0.2202
0.000800	0.00900667	0.219676
0.001000	0.01129	0.219180
0.003000	0.0321468	0.214751
0.005000	0.0511581	0.210867
0.007000	0.0696323	0.207225
0.008000	0.0785532	0.205511
0.009000	0.0875228	0.203816
0.010000	0.0964584	0.202155
0.020000	0.185889	0.18691
0.025000	0.231756	0.1799500

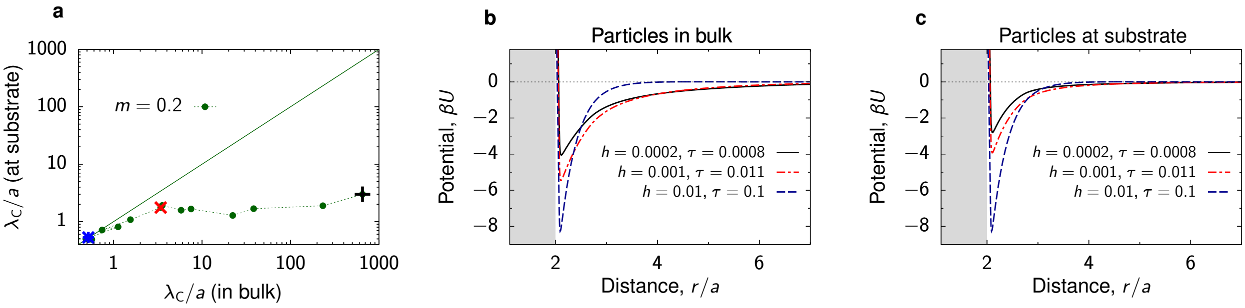

FIG. S2. **Interaction between nanoparticles in bulk and at a substrate in a near-critical fluid.** (**a**) Decay length of critical Casimir interactions at substrate and in bulk along the path $m = 0.2$ (Fig. S1 and Table S1). The particle and the substrate prefer the same phase of the fluid. The symbols show the points used in the remaining panels. (**b,c**) Total interaction potential comprises the critical Casimir, short-range soft repulsion and Debye-screened electrostatic repulsion. The reduced temperature $\tau = (T - T_c)/T_c$ and the bulk magnetic field h of the Ising model are varied such that the bulk magnetization is constant $m = 0.2$. The Debye screening length $\lambda_D = a$, where a is the nanoparticle radius.

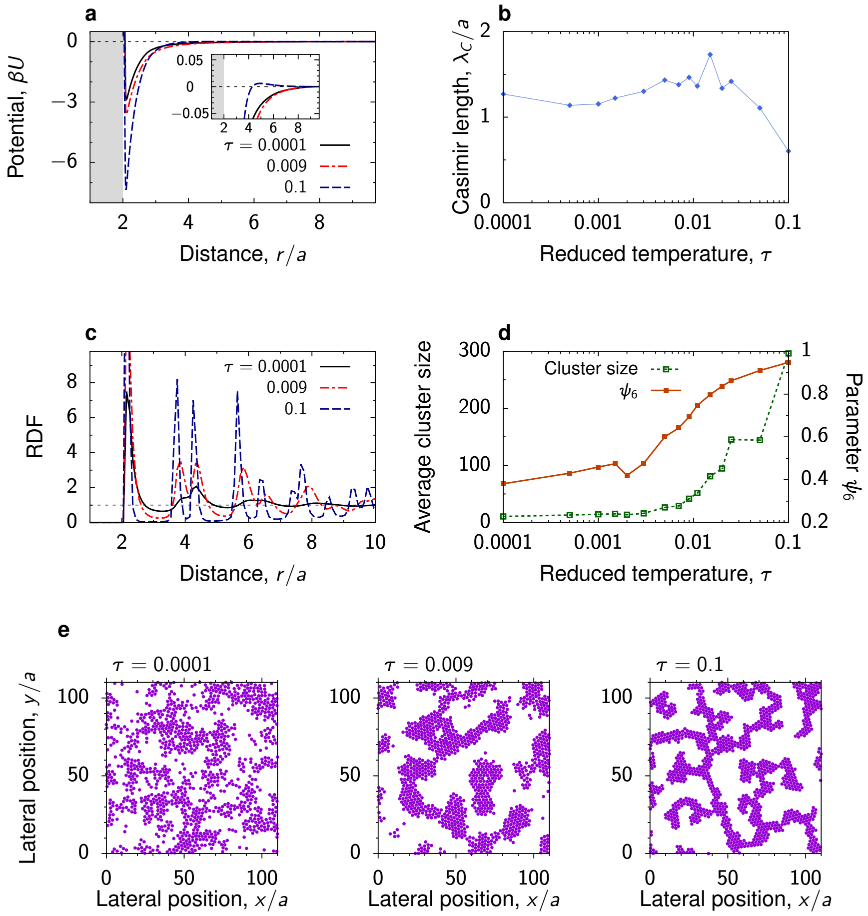

FIG. S3. **Nanoparticle interactions and structures at the critical composition (zero bulk field of the Ising model).** (**a**) Total interaction potential between two identical nanoparticles at a substrate in a near-critical fluid. The particles and the substrate favor the same fluid component. (**b**) Decay length of the critical Casimir potential as a function of the reduced temperature $\tau = (T - T_c)/T_c$, where T_c is the critical temperature. (**c**) Radial distribution functions (RDFs) and (**c**) cluster size distributions in the systems with the interaction potentials from panel (a) obtained by 2D molecular dynamics (MD) simulations. (**d**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of τ. (**e**) Snapshots from MD simulations for three values of τ. In all plots the Debye screening length $\lambda_D/a = 1$, bulk field of the Ising model $h = 0$ and the surface packing fraction $\eta = 0.3$.

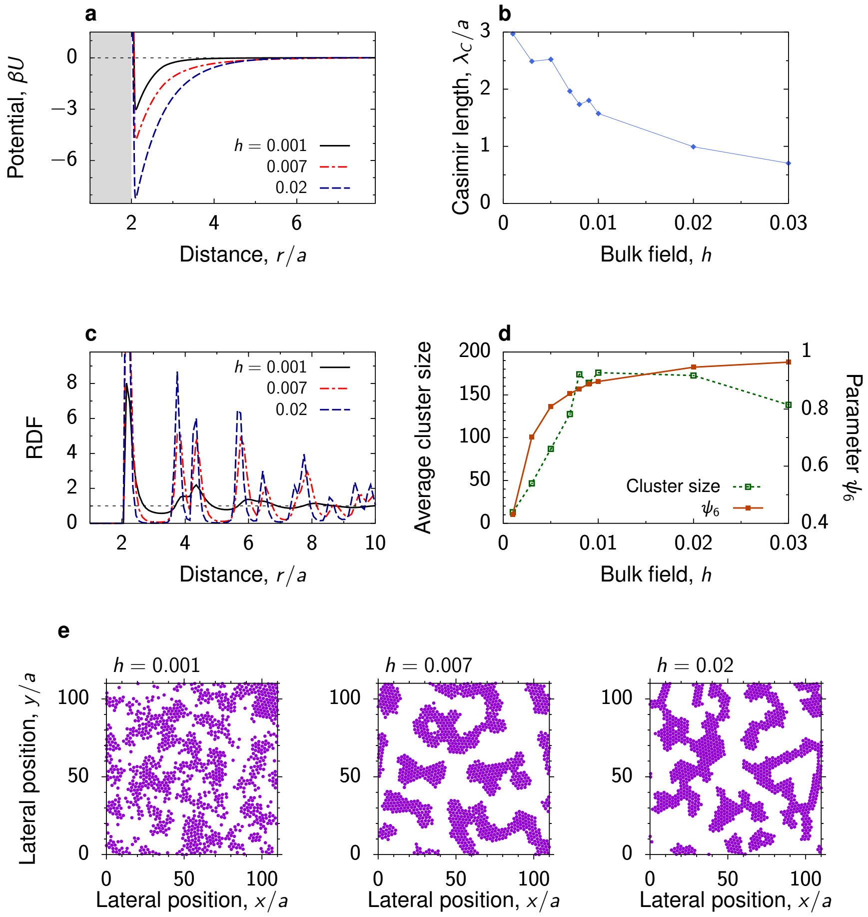

FIG. S4. **Nanoparticle structures along the path of constant reduced temperature.** (**a**) Total interaction potential between two identical nanoparticles at a substrate in a near-critical fluid. The particles and the substrate favor the same fluid component. (**b**) Decay length of the critical Casimir potential as a function of bulk field h. (**c**) Radial distribution functions (RDFs) and (**c**) cluster size distributions in the systems with the interaction potentials from panel (a) obtained by 2D molecular dynamics (MD) simulations. (**d**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of h. (**e**) Snapshots from MD simulations for three values of h. In all plots the Debye screening length $\lambda_D/a = 2$, reduced temperature $\tau = 0.007$ and the surface packing fraction $\eta = 0.3$.

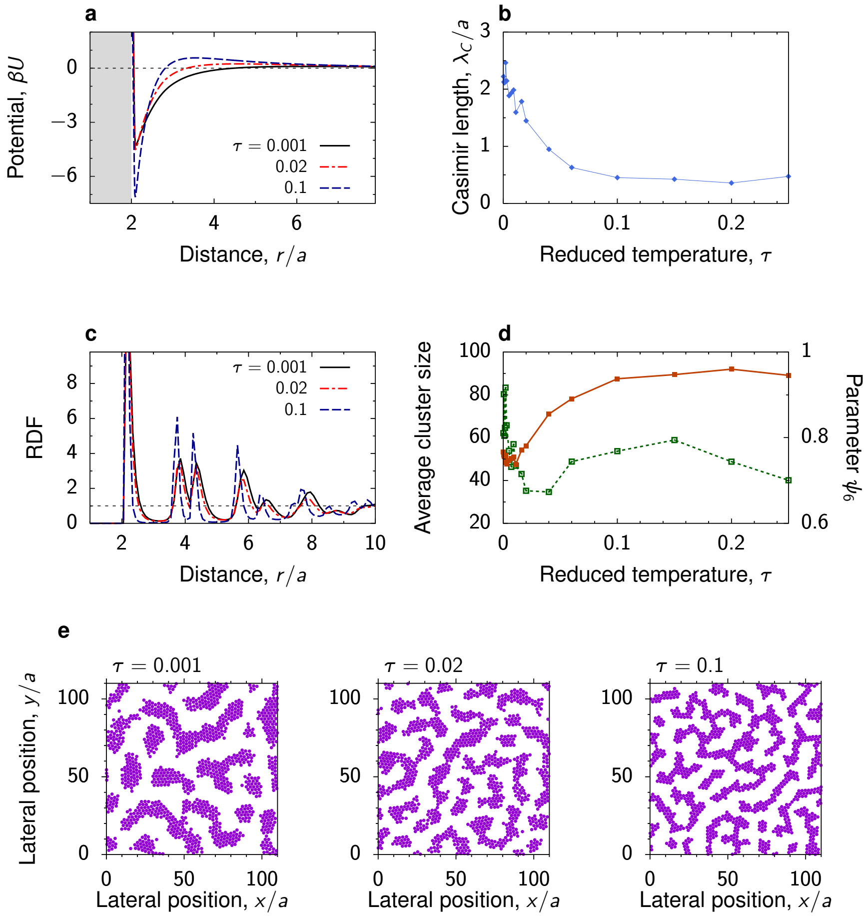

FIG. S5. **Nanoparticle structures along the path of constant bulk field of the Ising model.** (**a**) Total interaction potential between two identical nanoparticles at a substrate in a near-critical fluid. The particles and the substrate favor the same fluid component. (**b**) Decay length of the critical Casimir potential as a function of the reduced temperature $\tau = (T - T_c)/T_c$, where T_c is the critical temperature. (**c**) Radial distribution functions (RDFs) and (**c**) cluster size distributions in the systems with the interaction potentials from panel (a) obtained by 2D molecular dynamics (MD) simulations. (**d**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of τ. (**e**) Snapshots from MD simulations for three values of τ. In all plots the Debye screening length $\lambda_D/a = 4$, bulk field of the Ising model $h = 0.007$ and the surface packing fraction $\eta = 0.3$.

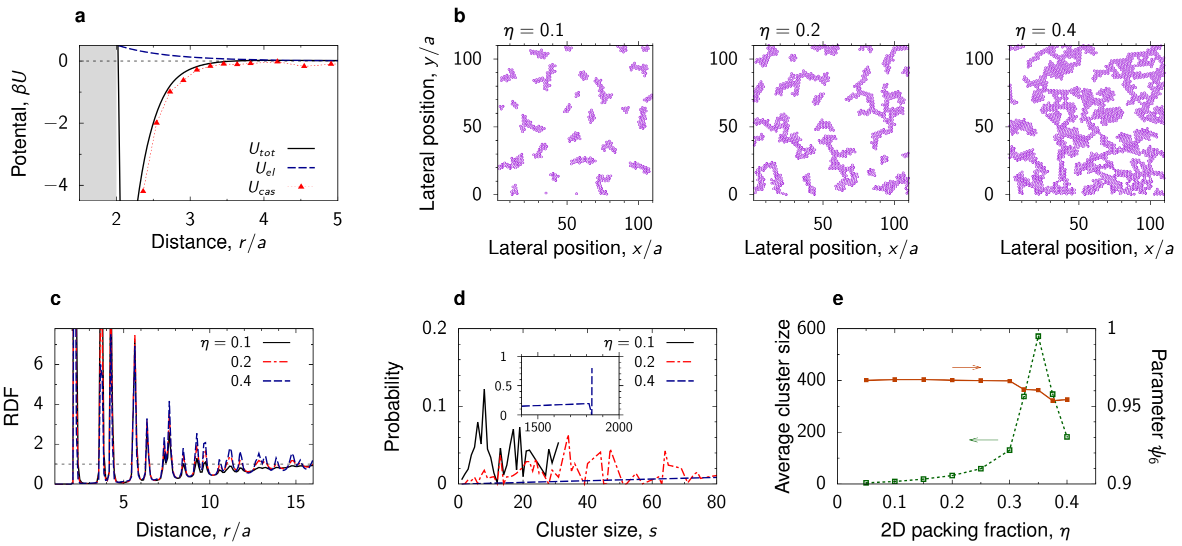

FIG. S6. **Effect of nanoparticle density: $\lambda_D/a = 1$, $\lambda_C/a = 0.49$.** (**a**) Electrostatic, critical Casimir and the total interaction potential between two nanoparticles at a substrate in a near-critical fluid. The substrate and the particles prefer the same fluid component. (**b**) Snapshots from MD simulations for a few values of the two-dimensional packing fraction $\eta = \pi N a^2/A$, where N is the number of particles, A the surface area and a the particle radius. (**b**) Radial distribution functions and (**c**) cluster size distributions for the same systems. (**d**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of η. The reduced temperature $\tau = 0.19$ and bulk field $h = 0.02$ giving the bulk magnetization $m = 0.2$ and the decay length of the critical Casimir potential for nanoparticles at the substrate $\lambda_C/a \approx 0.49$. For a larger value of $\lambda_C > \lambda_D$ see Fig. S7, and Fig. 3 in the main text for the dependence on λ_C. The Debye screening length $\lambda_D/a = 1$.

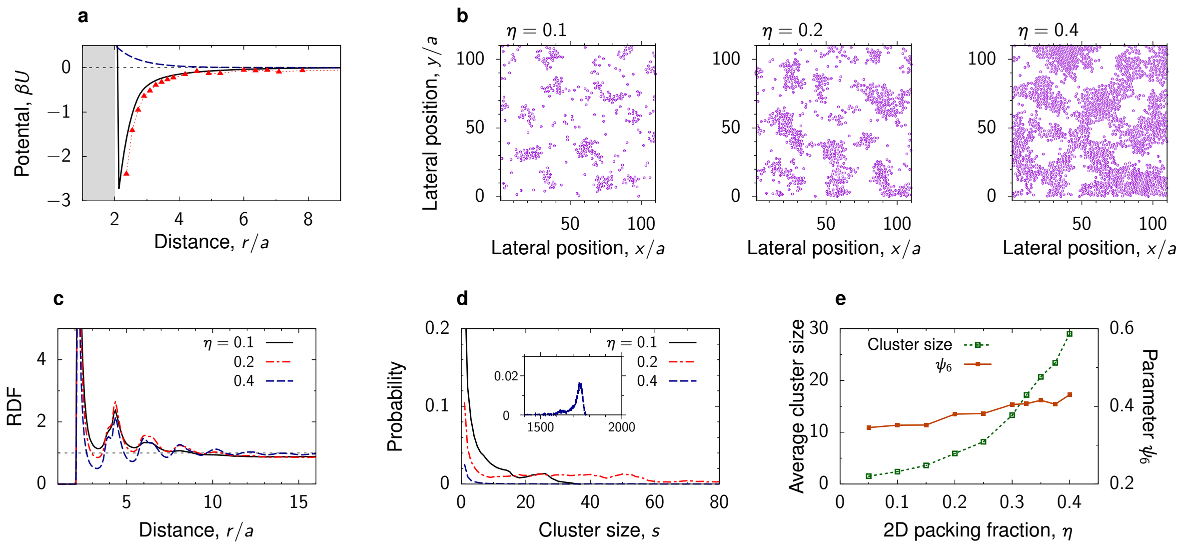

FIG. S7. **Effect of nanoparticle density: $\lambda_D/a = 1$, $\lambda_C/a = 3$.** (**a**) Electrostatic, critical Casimir and the total interaction potentials between two nanoparticles at a substrate in a near-critical fluid. The substrate and the particles prefer the same fluid component. (**b**) Snapshots from MD simulations for a few values of the two-dimensional packing fraction $\eta = \pi N a^2/A$, where N is the number of particles, A the surface area and a the particle radius. (**c**) Radial distribution functions and (**d**) cluster size distributions for the same systems. (**e**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of η. The reduced temperature $\tau = 0.0008$ and bulk field $h = 0.0002$ giving the bulk magnetization $m = 0.2$ and the decay of the critical Casimir potential for nanoparticles at a substrate $\lambda_C/a \approx 3$. For a smaller value of λ_C see Fig. S6, and Fig. 3 in the main text for the dependence on λ_C. The Debye screening length $\lambda_D/a = 1$.

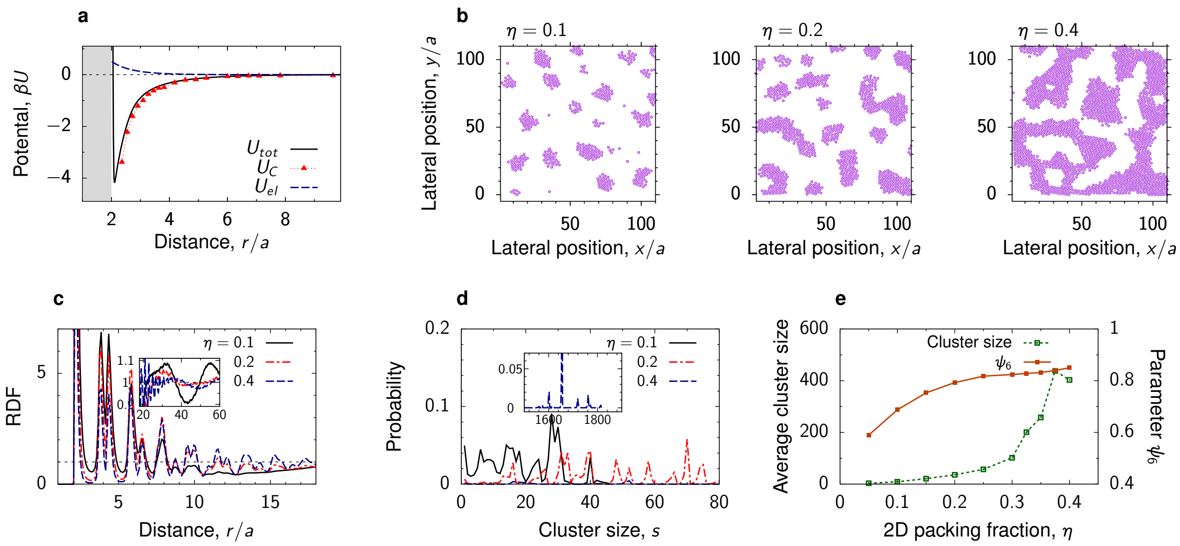

FIG. S8. **Effect of nanoparticle density: $\lambda_C/a = 2.5$, $\lambda_D/a = 1$.** (**a**) Electrostatic, critical Casimir and the total interaction potential between two nanoparticles at a substrate in a near-critical fluid. The substrate and the particles prefer the same fluid component. (**b**) Snapshots from MD simulations for a few values of the two-dimensional packing fraction $\eta = \pi N a^2/A$, where N is the number of particles, A the surface area and a the particle radius. (**b**) Radial distribution functions and (**c**) cluster size distributions for the same systems. (**d**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of η. The reduced temperature $\tau = 0.07$ and bulk field $h = 0.003$, giving the decay of the critical Casimir potential for nanoparticles at a substrate $\lambda_C/a \approx 2.5$ (Fig. 4 in the main text). The Debye screening length $\lambda_D/a = 1$. For higher values of λ_D see Figs. S9 and S10.

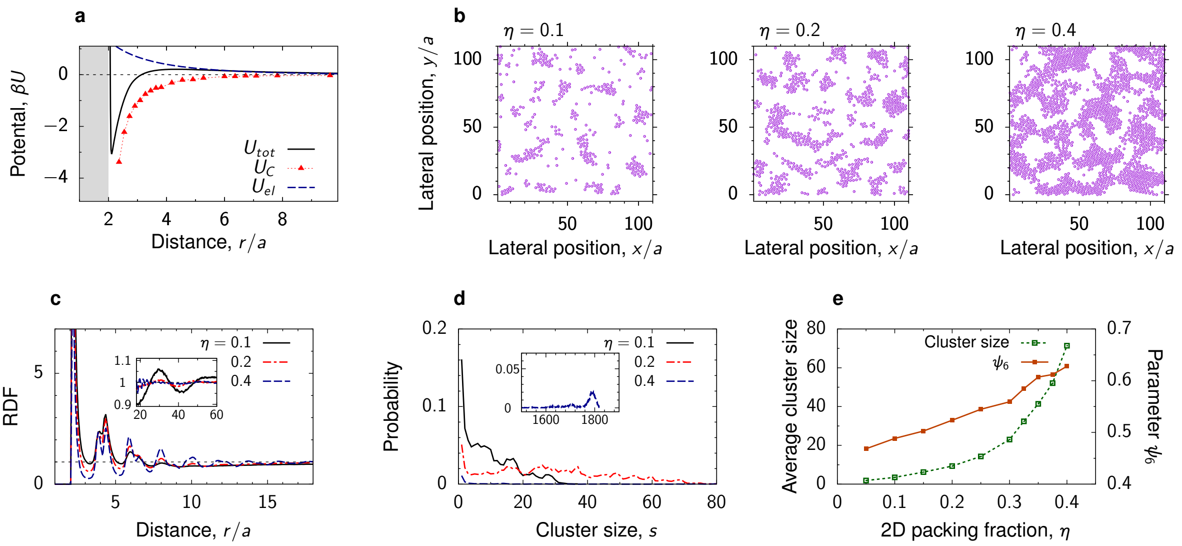

FIG. S9. **Effect of nanoparticle density:** $\lambda_C/a = 2.5$, $\lambda_D/a = 2.5$. (**a**) Electrostatic, critical Casimir and the total interaction potential between two nanoparticles at a substrate in a near-critical fluid. The substrate and the particles prefer the same fluid component. (**b**) Snapshots from MD simulations for a few values of the two-dimensional packing fraction $\eta = \pi N a^2/A$, where N is the number of particles, A the surface area and a the particle radius. (**b**) Radial distribution functions and (**c**) cluster size distributions for the same systems. (**d**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of η. The reduced temperature $\tau = 0.07$ and bulk field $h = 0.003$, giving the decay of the critical Casimir potential for nanoparticles at a substrate $\lambda_C/a \approx 2.5$ (Fig. 4 in the main text). The Debye screening length $\lambda_D/a = 2.5$. For other values of λ_D see Figs. S8 and S10.

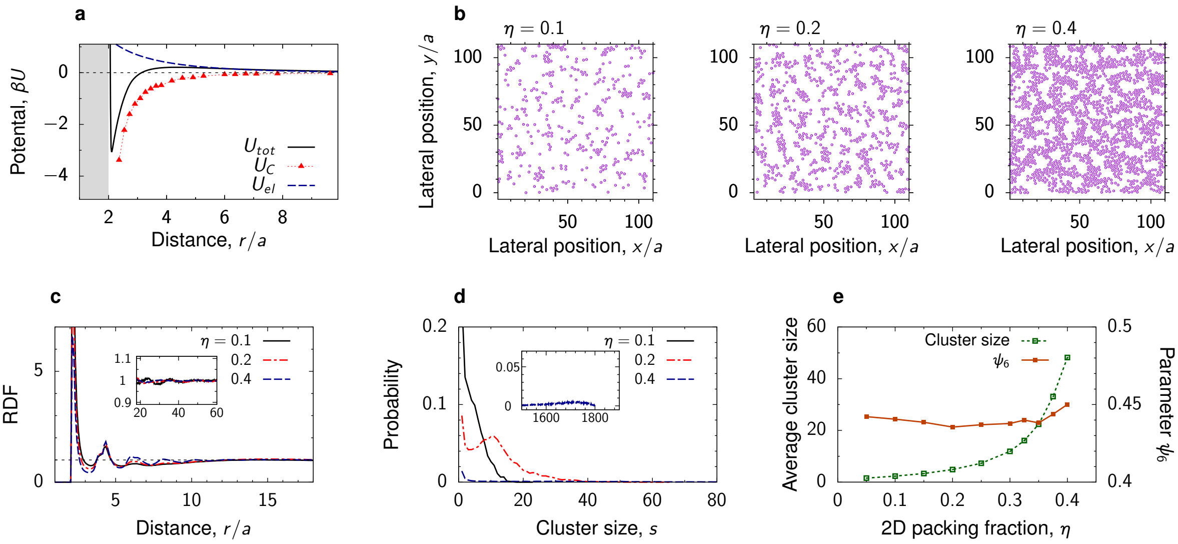

FIG. S10. **Effect of nanoparticle density: $\lambda_C/a = 2.5$, $\lambda_D/a = 4$.** (**a**) Electrostatic, critical Casimir and the total interaction potential between two nanoparticles at a substrate in a near-critical fluid. The substrate and the particles prefer the same fluid component. (**b**) Snapshots from MD simulations for a few values of the two-dimensional packing fraction $\eta = \pi N a^2/A$, where N is the number of particles, A the surface area and a the particle radius. (**b**) Radial distribution functions and (**c**) cluster size distributions for the same systems. (**d**) Average cluster size and hexatic parameter ψ_6, eq. (7) in the main text, as functions of η. The reduced temperature $\tau = 0.07$ and bulk field $h = 0.003$, giving the decay of the critical Casimir potential for nanoparticles at a substrate $\lambda_C/a \approx 2.5$ (Fig. 4 in the main text). The Debye screening length $\lambda_D/a = 4$. For smaller values of λ_D see Figs. S8 and S9.

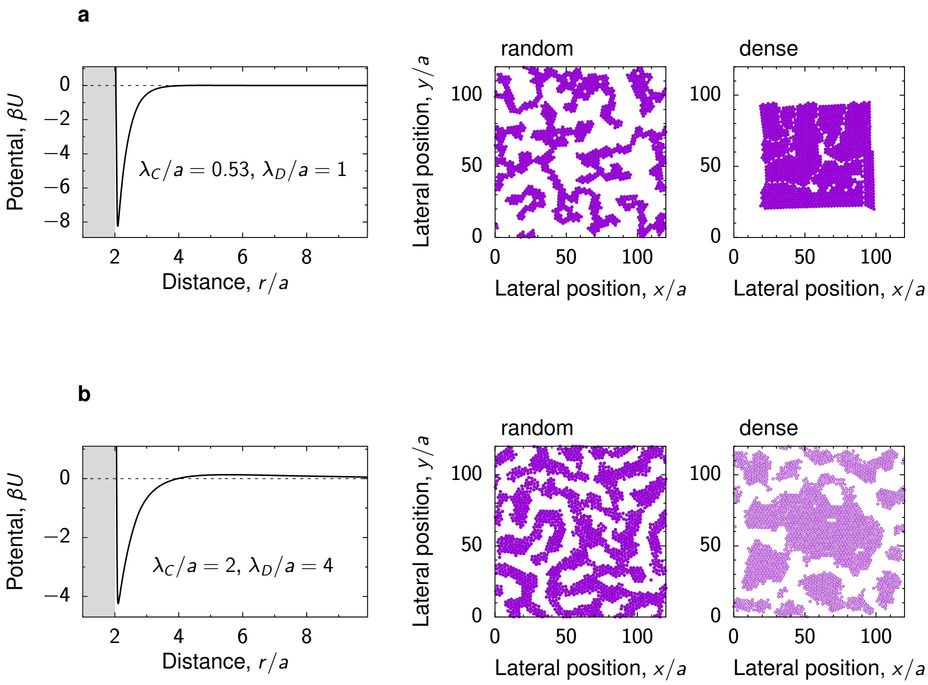

FIG. S11. **Effect of initial configuration.** Interaction potentials (left plots) and snapshots from the corresponding MD simulations (right plots). Nanoparticles were initially randomly distributed on the substrate (left snapshots) or densely packed (right snapshots). The model parameters are: (**a**) Debye screening length $\lambda_D/a = 1$, reduced temperature $\tau = 0.1$, bulk field $h = 0.01$ and the surface packing fraction $\eta = 0.3$ (fractal-like gels) and (**b**) $\lambda_D/a = 4$, $\tau = 0.007$, $h = 0.007$ and $\eta = 0.4$ (bicontinuous phase). A large cluster with defects forms in (a) when starting from a densely packed configuration. In (b) the cluster breaks and the system evolves towards the structure consistent with the one obtained from the random configuration. For random initial configurations, the simulation times were $100\tau_d$, where $\tau_d = a^2/D$ is the diffusion time, D the diffusion coefficient and a the particle radius. For dense initial configurations, the simulations lasted 5 times longer.

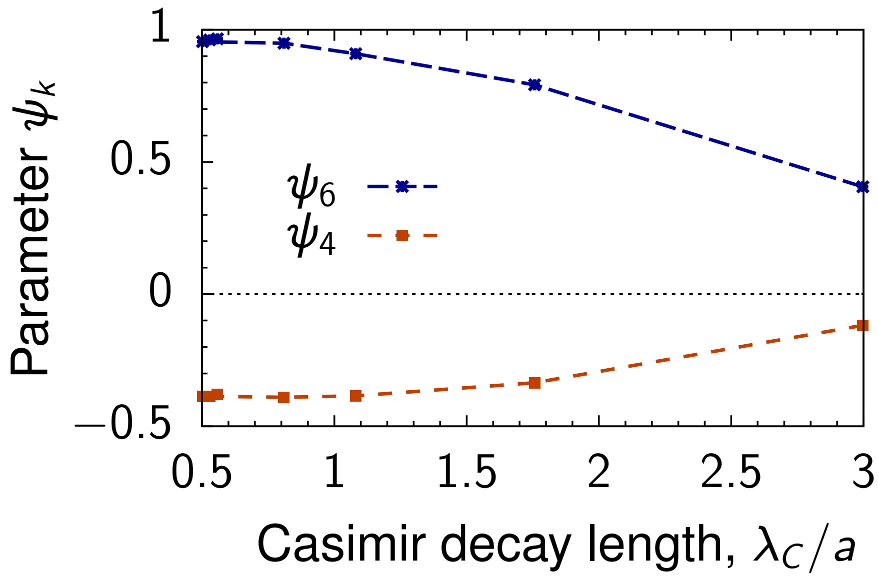

FIG. S12. **Order parameter** ψ_4 *versus* ψ_6**.** The parameters describe quadratic and hexagonal ordering of nanoparticles and are shown as functions of the decay length λ_C of the critical Casimir interactions between two nanoparticles at a substrate, all immersed in a near-critical fluid. The substrate and the particles prefer the same fluid phase. The Debye screening length $\lambda_D/a = 1$ and surface packing fraction $\eta = 0.3$. The parameters were obtained from 2D molecular dynamics simulations. For details see Fig. 3 in the main text.

TABLE S2. **Debye lengths and the amplitude of the Debye-screened electrostatic interactions used in our molecular dynamics simulations.** A_{el} was calculated according to eq. (5) of the main text. The second column was calculated using the nanoparticles radius $a = 2.75\,\mathrm{nm}$.

λ_D/a	λ_D (nm)	A_{el}
0.5	1.375	0.65
1	2.75	1.47
2	5.5	2.61
3	8.25	3.3
4	11	3.75
5	13.75	4.07
6	16.5	4.31
7	19.25	4.49
8	22	4.63
10	27.5	4.85
12	33	5
15	41.25	5.16