# Nonadditive Interactions and Phase Transitions in Strongly Confined Colloidal Systems: Electronic Supplementary Information.

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## S1. MEAN FIELD THEORY

We describe a critical fluid by its continuous order-parameter field  $\varphi(\mathbf{r})$ , where  $\mathbf{r}$  is a position vector. The free energy of the system is  $-k_BT \ln \mathcal{Z}$  with the partition function

$$\mathcal{Z} = \int \mathcal{D}\varphi \, \mathrm{e}^{-\mathcal{H}[\varphi]},\tag{1}$$

where  $\mathcal{D}\varphi$  denotes the functional integral over  $\varphi(\mathbf{r})$  and

$$\mathcal{H}[\varphi] = \frac{1}{V} \int_{V} d^{d}r \left\{ \frac{1}{2} (\nabla \varphi(\boldsymbol{r}))^{2} + \frac{\tau}{2} \varphi^{2}(\boldsymbol{r}) + \frac{g}{4!} \varphi^{4} + h \varphi(\boldsymbol{r}) \right\}$$
(2)

is the Ginzburg-Landau-Wilson (LGW) Hamiltonian for the Ising universality class. Here  $d^d r = \prod_{\alpha=1}^d dx_\alpha$  is the *d*-dimensional volume element, *h* is the external bulk field,  $\tau$  is proportional to the reduced temperature *t*, and *V* is the volume of the system.

In view of the difficulties to calculate  $\mathcal{Z}$ , frequently a saddle point (mean field) approximation is used, in which the integral in eqn (1) is determined approximately by taking into account only the most probable order-parameter configuration. Effectively this amounts to minimizing the LGW Hamiltonian. Even this minimization can be carries out analytically only for a few simple cases, whereas for the complicated geometry studied here we have to resort to numerical calculations. This numerical minimization of  $\mathcal{H}[\varphi]$  has been carried out by using the finite element method in connection with the F3DM library [1, 2].

Having obtained the order-parameter profiles for the setup of Fig. 1 (main text), the force between the colloids has been calculated based on the stress tensor [1, 3]

$$\mathcal{T}_{\alpha\beta} = \frac{\delta^2 \mathcal{H}}{\delta \partial_\alpha \varphi \, \delta \partial_\beta \varphi} - \delta_{\alpha\beta} \mathcal{H},\tag{3}$$

where  $\partial_{\alpha} = \partial/\partial x_{\alpha}$  is the derivative with respect to the Cartesian coordinate  $\alpha$ ,  $\delta/\delta\partial_{\alpha}\varphi$  is a functional derivative, and  $\delta_{\alpha\beta}$  is the Kronecker symbol. We enclosed each colloid by an ellipsoidal, rather than spherical, surface  $(S_i)$  in order to avoid strong gradients of the order parameter close to the colloidal surfaces, where they can be computed only less accurately. The force acting on colloid i in direction  $\alpha$  follows from integrating the stress tensor over  $S_i$ , *i.e.*,

$$f_{i,\alpha} = \oint_{S_i} d^{d-1}s \sum_{\beta} \hat{\mathbf{n}}_{\beta} \mathcal{T}_{\beta\alpha}, \qquad (4)$$

where  $d^{d-1}s$  is the surface element on  $S_i$  and  $\hat{\mathbf{n}}$  is a unit vector normal to the surface and pointing towards the outside of  $S_i$ . Clearly, the lateral force acting on one colloid has the same magnitude but the opposite sign of the lateral force acting on the second colloid (Fig. 1, main text); thus in all figures the force  $f \equiv f_x = (f_{1,x} - f_{2,x})/2$  acting on colloid 1 is presented. (Due to thermal equilibrium, Newton's third law holds even for effective forces like the one here.)



FIG. S1. (a) Cross-section of the MFT order parameter (OP,  $\varphi$ ) distribution through the centers of the colloids for the [+(-)+] configuration of the boundary conditions. The OP is normalized by its amplitude  $\mathcal{A}$  in the bulk (*i.e.*, for the unconfined) system with no colloids. The white lines are isolines corresponding to  $\varphi = 0$ . The upper panel corresponds to D/R = 2.5 (no-bridge state). The bottom one corresponds to D/R = 2 (bridge state). In both panels one has  $\Omega = W/R = 3$ and  $\Theta_{-} = -2$ . Upon increasing  $\Delta = D/R$  the bridge dissolves, but we have not found any sign of a first-order phase transition between the bridge and the no-bridge configurations, *i.e.*, the transformation between these two states seems to occur continuously. (b) Attractive critical Casimir force within MFT between two colloids as shown in (a), normalized by the amplitude  $C_{+,+} = -283.61/g$  of the force scaling function for a slit with (+,+) boundary conditions at  $T_c$ and without colloids. (Here g > 0 is the coupling constant in the LGW Hamiltonian, see eqn (3) in the main text.) The system parameters in (b) are the same as in (a). The two red crosses in (b) indicate the values of  $\Delta$  used in panel (a). The curve does not exhibit any discontinuity of the force, which would signal a first-order bridging transition.



FIG. S2. MFT free energy scaling function for configurations with and without bridge (see Fig. 6 in the main text). The scaling function is normalized by the amplitude  $C_{+,+} = -283.61/g$  of the force scaling function for a slit with (+,+) boundary conditions at  $T_c$  and without colloids. The free energies are remarkably close to each other, suggesting that both configurations can coexist over a wide range of temperatures. The inset highlights the region where the bridge configuration starts to become unstable. The bridge and no-bridge configurations coincide close to the critical point ( $\Theta = 0$ ), where the bridge starts to form (see Supplementary Video). These data correspond to the parameters  $\Delta = D/R = 0.8$  and  $\Omega = W/R = 3$  for the boundary configuration [+(-)+].

#### S2. MONTE CARLO SIMULATIONS

We consider an Ising model defined on a simple cubic lattice with lattice constant a. A classical spin  $\sigma_i = \pm 1$  is assigned to each lattice site i, which models an incompressible binary liquid mixture. Our goal is to study the effective interaction potential between two colloidal particles immersed in such a binary mixture in the additional presence of two confining walls. We thus consider a system of  $N_x \times N_y \times N_z$  lattice sites, which is periodic in the x and y directions. In z direction it has a width of  $W = N_z a$ . The Hamiltonian of such an Ising slit is

$$H(\{\sigma\}) = -J\sum_{\langle ij\rangle}\sigma_i\sigma_j + \sum_{\alpha\in\{\text{top,bot}\}}h_1^{\alpha}\sum_{k\in\alpha}\sigma_k,\tag{5}$$

where the interaction constant J = 1 if temperature T is measured in units of  $J/k_B$ , the sum  $\langle ij \rangle$  runs over all neighboring pairs of spins, and the second sum is over the spins at the slit walls. The surface fields  $h_1^{\text{bot}}$  and  $h_1^{\text{top}}$  act on the bottom and top layers, respectively. We consider the boundary conditions  $h_1^{\alpha} = \pm \infty$  ( $\alpha \in \{\text{top, bot}\}$ ), which correspond to the so-called normal surface universality class [4, 5]. This means that the spins on the sites nearest to the walls are fixed to the values dictated by  $h_1^{\alpha}$  (*i.e.*,  $\pm 1$  for  $h_1^{\alpha} = \pm \infty$ ).

The free energy of the system (without colloids) is

$$\mathcal{F}_{\rm slit}(\beta, W) = -\frac{1}{\beta} \ln \left[ \sum_{\{\sigma\}} e^{-\beta H(\{\sigma\})} \right], \tag{6}$$

where  $k_{\rm B}\beta = 1/T$  is the inverse temperature, and the sum runs over all spin configurations  $\{\sigma\}$ .

In order to introduce a quasi-spherical colloidal particle on a lattice, we first draw a sphere of radius R around a selected lattice site, which coincides with the center of the colloid [6, 7]. All spins within this sphere are considered as belonging to the colloidal particle and are fixed to  $\sigma = \sigma_{col}$  (= ±1 depending on the surface field). As for the slit walls, we consider the case of strong surface fields,  $h_1^{col} = \pm \infty$ . This implies that any neighboring spin  $\sigma_j$ , which is in contact with the colloid, is frozen, too, and hence  $\sigma_j = \sigma_{col}$ . By convention the colloidal radius is [6, 7]  $R = (N_R + 1/2)a$ , where  $N_R$  is the number of spins which belong to the colloid along an arbitrary axis.

With  $\{col\}\ denoting the set of all sites of frozen spins in the colloidal system,$ *i.e.*, of the spins of the two colloidal particles plus their neighboring spins, the free energy of the system

with two colloids – their centers being located in the mid-plane of the slit – is

$$\mathcal{F}_{2}(\beta, D, W, R) = -\frac{1}{\beta} \ln \left( \sum_{\{\sigma\}} \left[ \prod_{k \in \{\text{col}\}} \delta_{\sigma_{k}, \sigma_{\text{col}}} \right] e^{-\beta H(\{\sigma\})} \right).$$
(7)

Here, the product of Kronecker deltas  $\delta_{\sigma_k, \text{col}}$  fixes the values  $\sigma_k$  of the spins for  $k \in \{\text{col}\}$ . The free energy of insertion of two colloids into the Ising slit is

$$\Delta \mathcal{F}_2(\beta, D, W, R) = \mathcal{F}_2(\beta, D, W, R) - \mathcal{F}_{\text{slit}}(\beta, W).$$
(8)

In order to compute  $\Delta \mathcal{F}$  we employed the numerical integration scheme over the local magnetization [7]. For an accurate integration we used the histogram re-weighting technique [8, 9]. Note that within this method it is not possible to calculate  $\mathcal{F}_2$  itself.

The effective Ising spin mediated interaction potential between the two colloids (*i.e.*, the critical Casimir potential) is given by

$$\phi(\beta, D, W; D_{\max}, R) = \Delta \mathcal{F}_2(\beta, D, W, R) - \Delta \mathcal{F}_2(\beta, D_{\max}, W, R), \tag{9}$$

where  $D_{\text{max}} = N_x a/2 - 2R$  is the maximal possible distance between the two colloids in the system with  $N_x$  sites in the lateral direction x. As indicated  $\phi$  depends on  $D_{\text{max}}$ . However, we have checked that this dependence is negligible for large  $D_{\text{max}}$ . In all calculations we used  $D_{\text{max}} = 40a$  and checked that even for  $D_{\text{max}} = 20a$  the results practically coincide with the results for  $D_{\text{max}} = 40a$ .

### A. Test of universality of MC simulations

In view of limited computational resources, one has to consider relatively small colloidal particles. In particular, in most cases we simulated colloids of radius 5.5*a*, where *a* is the lattice constant of the Ising model. Such small systems are expected to exhibit a certain degree of non-universality. We have therefore checked that our system nevertheless reveals the universal behavior by comparing two systems of different sizes, one of which is obtained from the other by proportionally rescaling all lengths such that one obtains a desired ratio of colloidal radii. However, since our system is a discrete lattice, by doing so it is not possible to end up with unchanged values of the scaling variables  $\Delta = D/R$  and  $\Omega = W/R$  (and still having a computationally tractable system). Therefore, we had to limit these considerations



FIG. S3. Test of the scaling behaviour of the critical Casimir potential in units of  $k_B T$  as obtained from Monte Carlo simulations. The typical statistical inaccuracy is of the order of the symbol size. The scaling function  $\Phi$  of the potential is shown for two colloids of radius R = 5.5a (*a* is the lattice constant) and separation  $\Delta = D/R = 0.545$  as well as for radius R = 7.5a and separation  $\Delta = 0.533$  as a function of temperature  $\Theta = \Theta_{\pm} = \operatorname{sgn}(t) R/\xi_{\pm}$ , where  $\xi_{\pm} = \xi_0^{\pm} |t|^{\nu}$  is the bulk correlation length,  $\xi_0^{\pm}$  its amplitude for  $t \ge 0$ ,  $t = (T - T_c)/T_c$  with upper critical point  $T_c$ , and the critical exponent  $\nu \approx 0.63$ . The values of the slit width  $\Omega = W/R$  are indicated in the figure. Scaling is tested by comparing the data for (nearly) the same values of  $\Omega$  and  $\Delta$  but for distinct sizes R/a. Above  $T_c$  scaling is obtained, *i.e.*,  $\Phi$  is independent of the absolute value of R/a. Below  $T_c$  the red and the black data exhibit scaling, whereas the blue and the green data do so only to a lesser extent.

to values of  $\Delta = D/R$  and  $\Omega = W/R$ , which are only approximately equal to the original ones before the rescaling is carried out.

Our simulations show that the universal behavior is captured nevertheless (Fig. S3). The Casimir potentials practically coincide for the scaled systems in the vicinity of the critical point ( $\Theta \rightarrow 0$ ). Larger deviations are only observed at temperatures well below  $T_c$ , where *a priori* universality is not expected to hold.



FIG. S4. MC data for bridge formation and critical Casimir potential in units of  $k_BT$ . (a) The order parameter distribution  $\varphi/\mathcal{A}$  normalized by the amplitude  $\mathcal{A} \simeq 1.692(4)$  [10] of the bulk OP below  $T_c$  for two colloid-colloid separations ( $\blacksquare$  and  $\blacktriangle$ , see (b)) featuring a no-bridge and a bridge state, respectively. (b) Critical Casimir potential obtained from Monte Carlo simulations as a function of colloid-colloid separation. The potential in units of  $k_BT$ , *i.e.*,  $\Phi$  is shown for colloids of radius R = 5.5a (*a* is the lattice constant), slit width  $\Omega = W/R \approx 3.45$ , and rescaled temperature  $\Theta_- = -0.513347$ . On the accessible scales,  $\Phi$  does not exhibit a break in slope, which would signal a first-order bridging transition.



FIG. S5. Critical Casimir potential between colloids as a function of the colloid-colloid separation  $\Delta = D/R$  from Monte Carlo simulations for the configuration [+(-)+] (see Fig. 1 in the main text). The critical Casimir potential is expressed in terms of  $k_BT$  (see eqn (2) in the main text). The plots in (a) and (b) are for two values of the temperature scaling variable  $\Theta_+ = R/\xi_+(t)$ . The centers of the colloids are located in the symmetry plane of the slit (see Fig. 1 in the main text). This figure shows that due to confinement also above  $T_c$  the absolute value of the potential is enhanced at small separations and weakened at large separations, although the magnitudes of these effects are smaller than below  $T_c$  (compare Fig. 4(b)).



FIG. S6. Critical Casimir potential  $\Psi$  for a single colloid of radius R in a slit of width W as function of the position z of the center across the slit with  $-W/(2R) + 1 < \zeta = z/R < W/(2R) - 1$ , as obtained from Monte Carlo simulations for the boundary configuration [+(-)+] (see Fig. 1 in the main text). The critical Casimir potential is expressed in units of  $k_BT$  (see eqn (2) in the main text). The colloid is strongly trapped in the middle of the slit. The trapping potential is chosen to be zero in the middle. This trapping potential is *de facto* independent of temperature, at least within the considered interval of rescaled temperatures.

#### S3. COLLOIDAL PHASE DIAGRAM

In order to study colloids immersed in a narrow slit filled by a critical fluid, we consider the case that they position themselves with their centers in the central symmetry plane of the slit. For opposite boundary conditions between the colloid and each wall of the [+(-)+]system, this is a weak constraint (Fig. S6). In this case, the effective dimensionality reduces to d = 2.

We express the grand canonical thermodynamic potential  $\mathcal J$  of the system as

$$\mathcal{J}[\rho] = \mathcal{U}[\rho] - T\mathcal{S}[\rho] - \mu \int d^2 r_{\parallel} \rho(\boldsymbol{r}_{\parallel}), \qquad (10)$$

where  $\mathbf{r}_{\parallel} = (x, y)$  is a two-dimensional position vector with  $d^2r_{\parallel} = dxdy$ ,  $\rho$  is the twodimensional number density of the colloids, and  $\mu$  their chemical potential; the integration is performed over the two-dimensional area accessible to the colloids. The first term in eqn (10) is the contribution to  $\mathcal{J}$  due to long-ranged interactions (in the present case the critical Casimir potential):

$$\mathcal{U}[\rho] \approx -\frac{1}{2} \int d^2 r_{\parallel} \int d^2 r'_{\parallel} C(\boldsymbol{r}_{\parallel}, \boldsymbol{r}'_{\parallel}) \rho(\boldsymbol{r}_{\parallel}) \rho(\boldsymbol{r}'_{\parallel}), \qquad (11)$$

where  $C(\mathbf{r}_{\parallel}, \mathbf{r}'_{\parallel}) = C(|\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel}|)$  is the direct correlation function, which we approximate as  $C(r_{\parallel}) \approx -\phi(r_{\parallel})H(r_{\parallel}-2\sigma)$ , where  $r_{\parallel} = |\mathbf{r}_{\parallel}|$  stands for  $|\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel}|$ . Here  $\phi$  is the critical Casimir potential,  $\sigma$  the hard disk radius, and H(x) the Heaviside step function. For a homogeneous system one has

$$\mathcal{U}(\rho) \approx \frac{A}{2} \rho^2 \int_{r_{\parallel} > 2\sigma} d^2 r_{\parallel} \phi(r_{\parallel}), \qquad (12)$$

where A is the surface area of one slit wall. We incorporate repulsive electrostatic interactions between charged colloids into the hard core reference system, so that  $\sigma > R$ , where R is the colloidal radius used in our critical Casimir studies (see eqn (1) in the main text).

Concerning the entropic contribution we resort to scaled particle theory. Within this approach the entropy is approximated as [11, 12]

$$\mathcal{S}[\rho] \approx -k_B A \left\{ \rho \ln \left(\rho/\rho_{\text{ref}}\right) + \rho \left[\frac{\eta}{1-\eta} - \ln(1-\eta)\right] \right\},\tag{13}$$

where  $\rho_{\text{ref}}$  is a reference density. The first term in eqn (13) is the ideal gas contribution and  $\eta = \pi \rho \sigma^2$  is the two-dimensional colloidal packing fraction.

Combining Eqs. (10), (12), and (13), we obtain the following dimensionless expression for a homogeneous two-dimensional system:

$$\tilde{\mathcal{J}}(\eta) = \pi \sigma^2 \beta \mathcal{J}/A = \frac{U_0 \eta^2}{2\pi} + \eta \left[ -\tilde{\mu} + \frac{\eta}{(1-\eta)} + \ln \frac{\eta}{(1-\eta)} \right],\tag{14}$$

where  $\tilde{\mu} = \beta \mu + \ln(\pi \sigma^2 \rho_{\rm ref})$  and

$$U_0 = \frac{2\pi\beta}{\sigma^2} \int_{2\sigma}^{\infty} dr_{\parallel} r_{\parallel} \phi(r_{\parallel}) = \frac{8\pi}{\left(2 + \Delta_{\min}\right)^2} \int_{\Delta_{\min}}^{\infty} \Phi(\Theta, \Delta) (2 + \Delta) d\Delta, \tag{15}$$

where  $\Phi(\Theta, \Delta)$  is the critical Casimir potential scaling function (see eqn (2) in the main text),  $\Delta = D/R = r_{\parallel}/R - 2$  and  $\Delta_{\min} = 2(\sigma - R)/R$  is the minimal surface-to-surface distance between the colloids, which we take to be larger than 2*R* due to the presence of short-ranged repulsive electrostatic interactions. In order to determine  $\Delta_{\min}$  we resort to Rowlinson's expression for an effective hard sphere diameter [13]:

$$\Delta_{\min} = \frac{1}{R} \int_0^\infty \left( 1 - e^{-\beta \phi_{\text{short}}(D)} \right) dD, \qquad (16)$$

where  $\phi_{\text{short}}(D)$  is the interaction energy between charged colloids, for which we adopt the Debye-Hückel (DLVO) form [14]

$$\phi_{\rm short}(D) = \frac{l_B Z^2}{(1 + \varkappa R)^2} \frac{e^{-\varkappa D}}{D + 2R},$$
(17)

where Z is the colloidal charge (in units of the elementary charge e),  $l_B = \beta e^2/(4\pi\varepsilon_0\varepsilon_r)$  is the Bjerrum length ( $\varepsilon_0$  is the vacuum permittivity and  $\varepsilon_r$  is the relative dielectric constant), and  $\varkappa$  is the inverse of the Debye screening length. We note that this ansatz neglects the effect of the slit walls on the electrostatic colloid-colloid interactions, which we expect to be negligible for uncharged non-conducting walls; for charged walls, however, this many-body effect can be significant [15, 16] and remains to be considered in future studies.

We have used the following parameters in Fig. 5: colloid radius R = 250 nm,  $l_B = 0.7$  nm (Bjerrum length in water); Debye screening length  $\varkappa^{-1} = 5$  nm, which corresponds to an electrolyte concentration of 4 nM at T = 312 K (which is the critical temperature of the 3-methyl-pyridine/heavy water mixture); colloidal charge  $Z = 1.3 \times 10^4$ , which corresponds to a surface charge density of 0.26  $\mu$ C/cm<sup>2</sup>. These parameters lead to  $\Delta_{\min} \approx 0.1$ , which corresponds to an effective hard disk radius  $\sigma \approx 262$  nm (for R = 250nm). For reasons of simplicity we consider  $\Delta_{\min}$  to be independent of temperature and slit width.



FIG. S7. The parameter  $U_0$  of the random phase approximation as function of the rescaled temperature  $\Theta = R/\xi(t)$  for  $T > T_c$  (see eqn (15) of Section S3 in ESI and eqn (2) in the main text). The colloidal hard disk radius is R = 5.5a where a is the lattice constant of the underlying Ising model, which is used to determine via MC simulations the critical Casimir potential scaling function  $\Phi$  entering into eqn (15) of Section S3 in ESI; note that the dependence on temperature enters only via  $U_0$  through this equation. The minimal surface-to-surface distance between the colloids is  $\Delta_{\min} = 0.1R$  due to short-ranged electrostatic repulsion (see Section S3 in ESI). The thin horizontal line shows the colloidal critical value  $U_0^{cc}/(2\pi) \approx -5.84$ . The colloidal critical temperatures in Fig. 5 of the main text have been inferred approximately from this plot by solving graphically  $U_0(\Theta) = U_0^{cc}$ .

The scaling function  $\Phi$  of the critical Casimir potential was obtained by MC simulations (Section S2 in ESI) and the subsequent integration in eqn (15) was performed by first fitting the data to  $U_{fit} = A_{Cas} e^{-\varkappa_{Cas}D}$  and then by integrating this expression analytically.  $U_{fit}$  is a fairly good approximation because here the system is well above the fluid critical point. The dependence of  $U_0$  on the temperature scaling variable  $\Theta$  is shown in Fig. S7.

We have used our own code together with the GNU Scientific Library [17] in order to minimize the free energy  $\tilde{\mathcal{J}}(\eta)$  numerically. The phase diagram was calculated by identifying the parameters for which  $\tilde{\mathcal{J}}$  has two coexisting minima, corresponding to low-density (colloidal gas) and high-density (colloidal liquid) states. The colloidal critical point of this model is at  $\eta_{cc} = (\sqrt{7} - 2)/3 \approx 0.215$  and  $U_0^{cc}/(2\pi) \approx -5.84$ . In Fig. S7  $U_0^{cc}$  is indicated by a thin horizontal line.

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