Supporting information for: Effective pair potential between charged nanoparticles at high volume fractions

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S1. Details of the OCM simulations

The One-Component Model (OCM) was simulated in the NVT ensemble with a classical Monte-Carlo method following the Metropolis algorithm, implemented in an in-house software. We used cubic splines to interpolate the tabulated effective potentials calculated from background charge simulations. The simulation box contained from 100 to 200 colloids (as in the full PM), the box length was set according to the studied volume fraction. 200000 Monte-Carlo cycles, consisting of N particle translation attempts, where N is the number of particles, were performed to equilibrate the dispersion. Additional 200000 cycles were used to produce the results, in particular the radial distribution functions.

S2. Details of the full Primitive Model simulations

We used the GROMACS software package (version 4.5.4) to perform the full Primitive Model simulations. The velocity–Verlet integrator was used with a time step of 10 fs. To make a correct sampling of the canonical ensemble we used the velocity–rescaling thermostat. We used Particle Mesh Ewald (PME) to compute electrostatic interactions, with a Fourier spacing of 1 nm and a real space cutoff of 18 nm. The simulations involved 200 colloids with the compensating 12000 monovalent ions, or 400 colloids with 12000 divalent ions. A starting configuration with random colloid and mobile ion coordinates was generated. The ions were then allowed to equilibrate, keeping the colloids fixed. Once the system energy was converged, all particles, including translation of the colloids, were allowed to move. Equilibration times of 1 ns were followed by production runs lasting 10 ns.

S3. Calculation of the electrostatic midplane force



Figure S1: $F_{back}^{el}(r, \phi)$ with monovalent counterions at $\phi = 3.3\%$ as a function of colloid separation. The red line is a fit to the computed values (black line with circles).

The inter-colloidal forces were calculated by evaluating the mean force over the midplane, which can be decomposed as (see main text)

$$F(r,\phi) = F^{el}(r,\phi) + F^{LJ}(r,\phi) + F^{id}(r,\phi) + F^{el}_{back}(r,\phi)$$
(1)

The last term, $F_{back}^{el}(r, \phi)$, is the average electrostatic force over the midplane of the background charge with the particles (colloids and small ions) and with itself. We solved it numerically from the calculation of the direct force applied to the colloids (insensitive to the background charge), whose computation is straightforward but has poorer statistics compared to the midplane calculations. The difference between the direct force and the calculated terms of the force over the midplane provides a first estimate of F_{back}^{el} . The latter is then collected as a function of colloid separation and finally fitted by a straight line to give the final values, see Figure S1.

S4. Calculated forces

Figure S2 and Figure S3 represent the forces between two colloids with monovalent and divalent counterions, respectively, as obtained from background charge simulations.



Figure S2: Inter-colloidal force with monovalent counterions calculated from background charge simulations for various particle volume fractions.



Figure S3: Inter-colloidal force with divalent counterions calculated from background charge simulations for various particle volume fractions.

The accuracy of the Fennell Hamiltonian to describe long range electrostatic interactions was also checked by performing force calculations using the Particle Mesh Ewald (PME) method. The simulations were performed at a particle volume fraction of 6.7 % using Molecular Dynamics with the GROMACS software package. In that case, only the direct force acting on the colloids was computed. One can see in Figure S4 which compares the intercolloidal force computed with PME and the Fennel Hamiltonian, that the mean forces are virtually the same within statistical uncertainties.



Figure S4: Inter-colloidal force with monovalent counterions at $\phi = 6.7\%$ obtained with the Fennell Hamiltonian (red crosses) and PME (black squares).

S5. Interactive Boltzmann Inverse calculations



Figure S5: Comparison between the inter-colloidal effective pair potential obtained from background charge simulations (thick lines) and interactive Boltzmann inverse simulations (thin lines with circles) for various particle volume fractions. The counterions are monovalent. The IBI potentials are not displayed down to the hard–core diameter, lacking good enough statistics for these small colloid separations.



Figure S6: Comparison between the inter–colloidal effective pair potential obtained from background charge simulations (thick lines) and interactive Boltzmann inverse simulations (thin lines with circles) for various particle volume fractions. The counterions are divalent.

From the radial distribution functions obtained from the full PM, one can estimate what is the optimum effective pair potential. One method to achieve this are interactive Boltzmann inverse calculations^{S1,S2} (IBI). Figures S5 and S6 compare the so obtained potentials with those computed from background charge simulations for monovalent and divalent counterions. For all volume fractions and ion types, the IBI potential is higher, confirming that our method tends to consistently overestimate the screening of the electrostatic repulsions.

References

- (S1) Reith, D.; Pütz, M.; Müller-Plathe, F. Deriving effective mesoscale potentials from atomistic simulations. *Journal of Computational Chemistry* 2003, 24, 1624–1636.
- (S2) Müller-Plathe, F. Coarse-Graining in Polymer Simulation: From the Atomistic to the Mesoscopic Scale and Back. *ChemPhysChem* 2002, *3*, 754–769.