

Supplementary information

The influence of surface roughness on the adhesive interactions and phase behavior of suspensions of calcite nanoparticles

Juan D. Olarte-Plata^a, Gøran Brekke-Svaland^a and Fernando Bresme^a

1 Probability distribution of surface heights

The continuous probability distribution for the surface heights follows a Gaussian distribution, given by:

$$f_h = \frac{e^{-(r-h)^2/(2\rho^2)}}{\rho\sqrt{2\pi}} \quad (1)$$

where r is the reference surface, h is the deviation with respect to r , and ρ is the surface roughness ($\rho = 0$ corresponds to a flat surface).

Fig. 1 shows the surface height distribution, with roughness $\rho = 0.3$ nm.

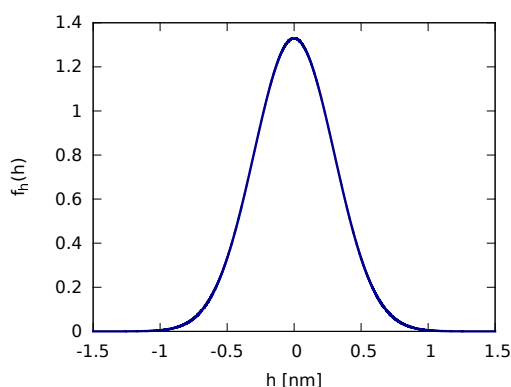


Fig. 1 Surface height distributions, with $\rho = 0.3$ nm.

2 Effective interparticle interactions

Fig 2 shows the effective inter-particle interactions in a longer range than that considered in Fig. 2D in the main document.

^a Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City Campus, 80 Wood Lane, London W12 0BZ, UK. E-mail: j.olarte@imperial.ac.uk, g.svaland15@imperial.ac.uk, f.bresme@imperial.ac.uk

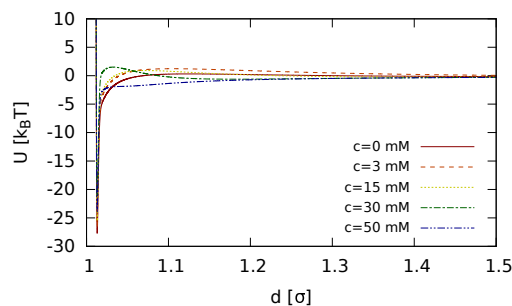


Fig. 2 Inter-particle interactions as a function of Ca(OH)_2 , in the range of inter-particle distance $1.0\sigma - 1.5\sigma$.

2.1 Particle size dependence of the effective interactions

The dependence of the effective interactions on the particle size is shown in Fig. 3. The increase of nanoparticle size results in an increase of the potential well depth, which has the consequence of increasing the minimum surface roughness required to stabilize the nanoparticle suspension. Larger particles featuring the same surface roughness, for instance $\rho = 1.5$ Å should therefore tend to aggregate with increasing adhesive energies.

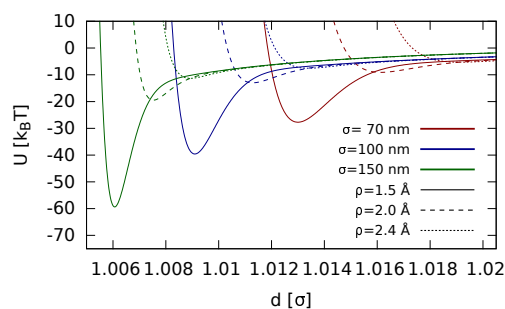


Fig. 3 Inter-particle interactions as a function of particle size σ and surface roughness ρ .

3 Langevin dynamics

To account for the stochastic collision of the solvent with the nanoparticles, and therefore Brownian motion, we used Langevin dynamics¹. In this method, a friction force and noise term are added to the equations of motion:

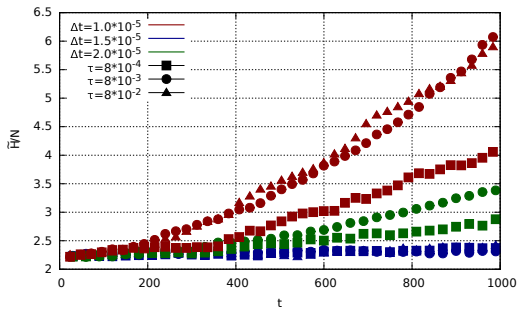


Fig. 4 Time evolution of the effective energy per particle, as a function of the timestep and the damping parameter, for the smooth potential of particles with $\sigma = 70\text{nm}$.

$$\frac{dx(t)}{dt} = v(t) \quad (2)$$

$$m \frac{dv(t)}{dt} = -\zeta v(t) - \frac{dU}{dt} + F(t) \quad (3)$$

where x and v are the position and velocity of a nanoparticle, m is its mass, ζ is the friction coefficient, U is the interaction energy between particles, and $F(t)$ is the stochastic noise term. This noise term fulfills $\langle F(t) \rangle = 0$ and $\langle F(t_1)F(t_2) \rangle = \Gamma(t_1 - t_2)$, where $\Gamma = 2\zeta k_B T$ quantifies the strength of the stochastic noise¹. We used the LAMMPS² implementation of the thermostat proposed by Bussi and coworkers³. In order to verify the accuracy of the integration, we used the effective energy conservation defined as³:

$$\tilde{H} = E_{tot} - \Delta E_{tstat} \quad (4)$$

where E_{tot} is the total energy of the system, and ΔE_{tstat} is the increment in energy due to the thermostat. We monitored the effective energy conservation for different values of timestep and damping parameters (see Fig. 4), for the interaction potential of particles with $\sigma = 70\text{nm}$, surface roughness $\rho = 1.5 \text{ \AA}$, and CaOH_2 concentration $c = 0 \text{ mM}$, which corresponds to the steepest and strongest attractive potential. We find effective energy conservation for $\Delta t = 1.0 \times 10^{-5}$, in a range of damping parameters 1-100 τ_{water} , where $\tau_{water} \approx 8 \times 10^{-4}$ in reduced units which corresponds to 0.8 ns in SI units, using the density of calcite 2710 kg/m^3 , and the nanoparticles of diameter 70 nm.

4 Calculation of fractal dimension

We present an example of the box counting algorithm, for the percolating gel shown in Fig. 3C in the main document. The system is divided in $N_b = 1, 2, 3 \dots$ segments on each dimension, and the number of filled boxes is counted. The log-scale plot of the number of filled boxes N_f as a function of L/l gives the fractal dimension, which is probed on the ranges of $l = [1\sigma, 5\sigma]$ for the local fractal dimension, and $l = [5\sigma, L]$ for the global fractal dimension. The variation in the slope at $\approx 5\sigma$ corresponds to the transition between the global structure of the cluster (*i.e.* its space-filling characteristics) and the local structure of the cluster.

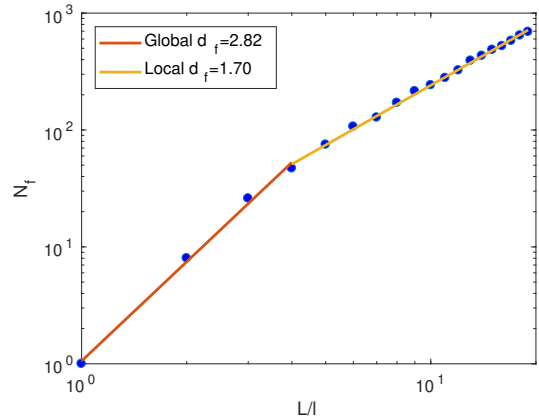


Fig. 5 Number of filled boxes as a function of the inverse of the box length normalized by the simulation cell size L , for the percolating cluster at $\phi = 0.07$, $\rho = 1.5 \text{ \AA}$ and CaOH_2 concentration $c = 30 \text{ mM}$ (shown in the main document as the structure in Fig. 3C). The global fractal dimension is calculated with the slope in the range $l = [5\sigma, L]$ and the local fractal dimension is calculated with the slope in the range $l = [1\sigma, 5\sigma]$.

References

- [1] N. Van Kampen, *Stochastic Processes in Physics and Chemistry*, North Holland Personal Library, 1981.
- [2] S. Plimpton, *Journal of Computational Physics*, 1995, **117**, 1–19.
- [3] G. Bussi and M. Parrinello, *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 2007, **75**, 1–7.