

Supporting Information for
Collective diffusive dynamics of charged nanoparticles in confinement

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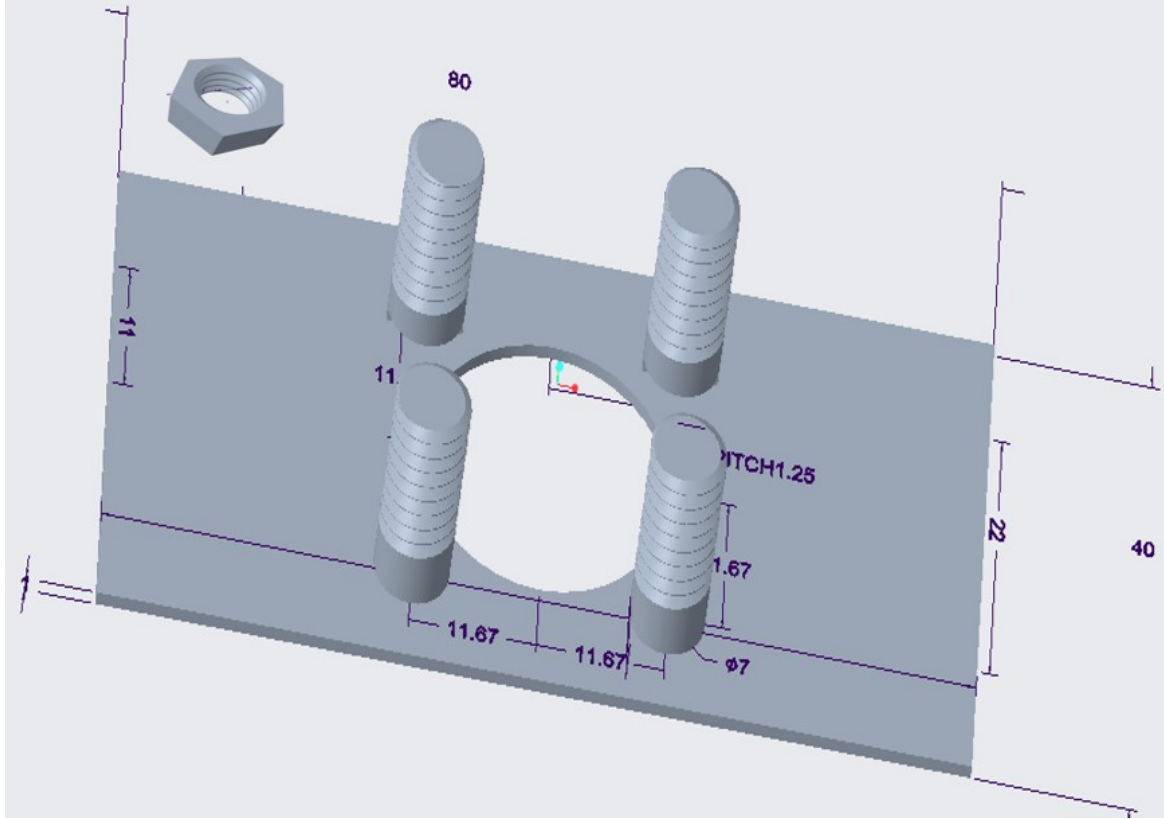


Figure S1 3D printed sample holder. Units are in mm.

Effective concentration:

Beer-Lambert's law ($I(h_o) = \epsilon l c^*$) was used to estimate the effective local concentration (c^*), which are presented in Figures S2d and S3. I is the local mean fluorescent intensity per pixel, ϵ is the coefficient of brightness, and l is the optical path length. l was approximated to be the local total confinement height (h_o) for different x values, where h_o was less than the resolution of the microscope objective ($\zeta \approx 400 \text{ nm}$). For radial position where h_o was greater than the objective resolution, l was approximated to be ζ . c^* was related to the bulk concentration (c) as follow:

$$c^* = \gamma c . \quad (1)$$

Where, γ is the activity coefficient that depends on the confinement height. Far away from contact point (e.g. $x = 2\text{mm}$, $h_o = 21.7 \mu\text{m}$), the local concentration approaches the bulk concentration. As a result, $\gamma \approx 1$. Moreover, at $x = 2\text{mm}$, the local fluorescent intensity can be related to the bulk concentration as follow:

$$I(h_o = 21.7 \mu\text{m}) = \varepsilon \zeta c \quad (2)$$

By plotting $I(h_o = 21.7 \mu\text{m})$ as a function of ζc for different bulk concentrations ($\varphi = 0.000005, 0.00001, 0.00005, 0.0001, 0.0005$), $\varepsilon (= 2209 \mu\text{m}^{-1})$ was obtained from the slope and does not depend on the confinement height. For other confinement heights, γ was computed using Eq.1 and the Beer-Lambert's law.

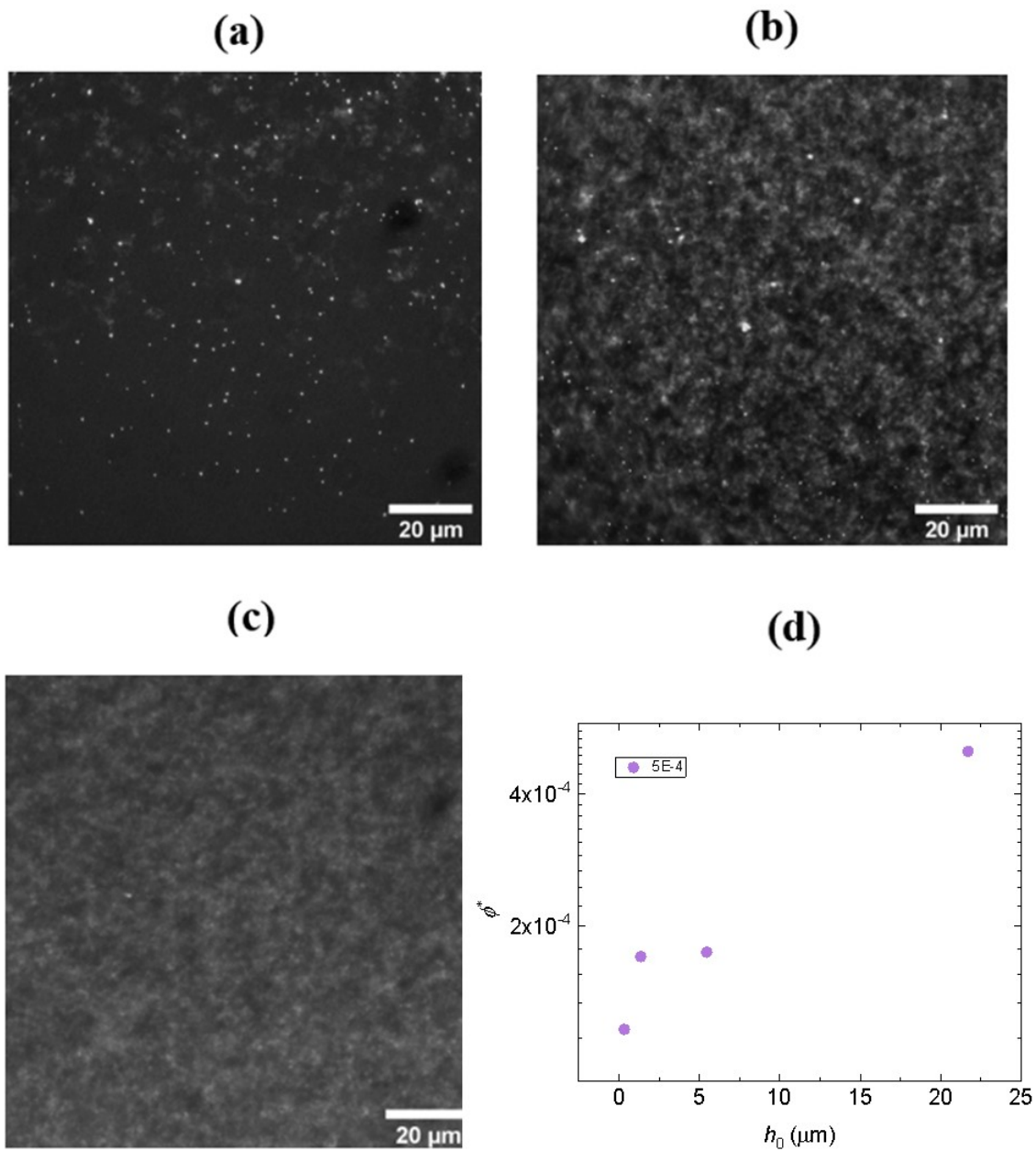


Figure S2 Concentration change as a function of radial position for $\phi = 0.00005$. (a) $x = 0.25$ mm, $h_o = 0.34 \mu\text{m}$ (b) $x = 0.5$ mm, $h_o = 1.34 \mu\text{m}$. (c) $x = 1$ mm, $h_o = 5.4 \mu\text{m}$. (d) Local concentration as a function of h_o .

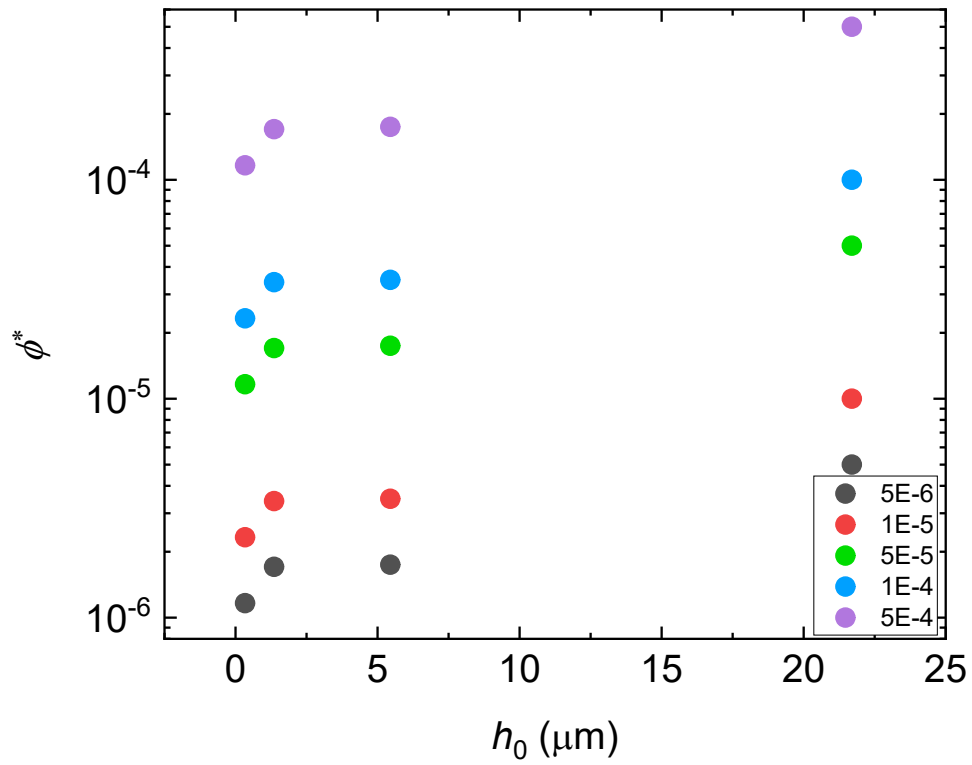


Figure S3 Local concentration change as a function of h_0 for different bulk concentrations.

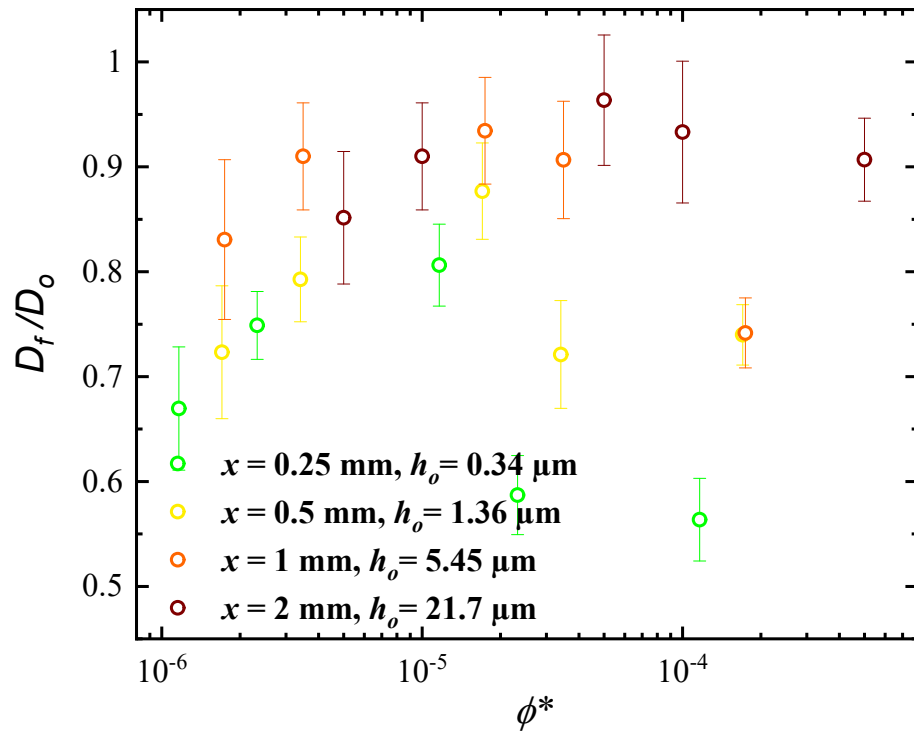


Figure S4 Mean relative diffusion coefficient change as a function of local concentration.

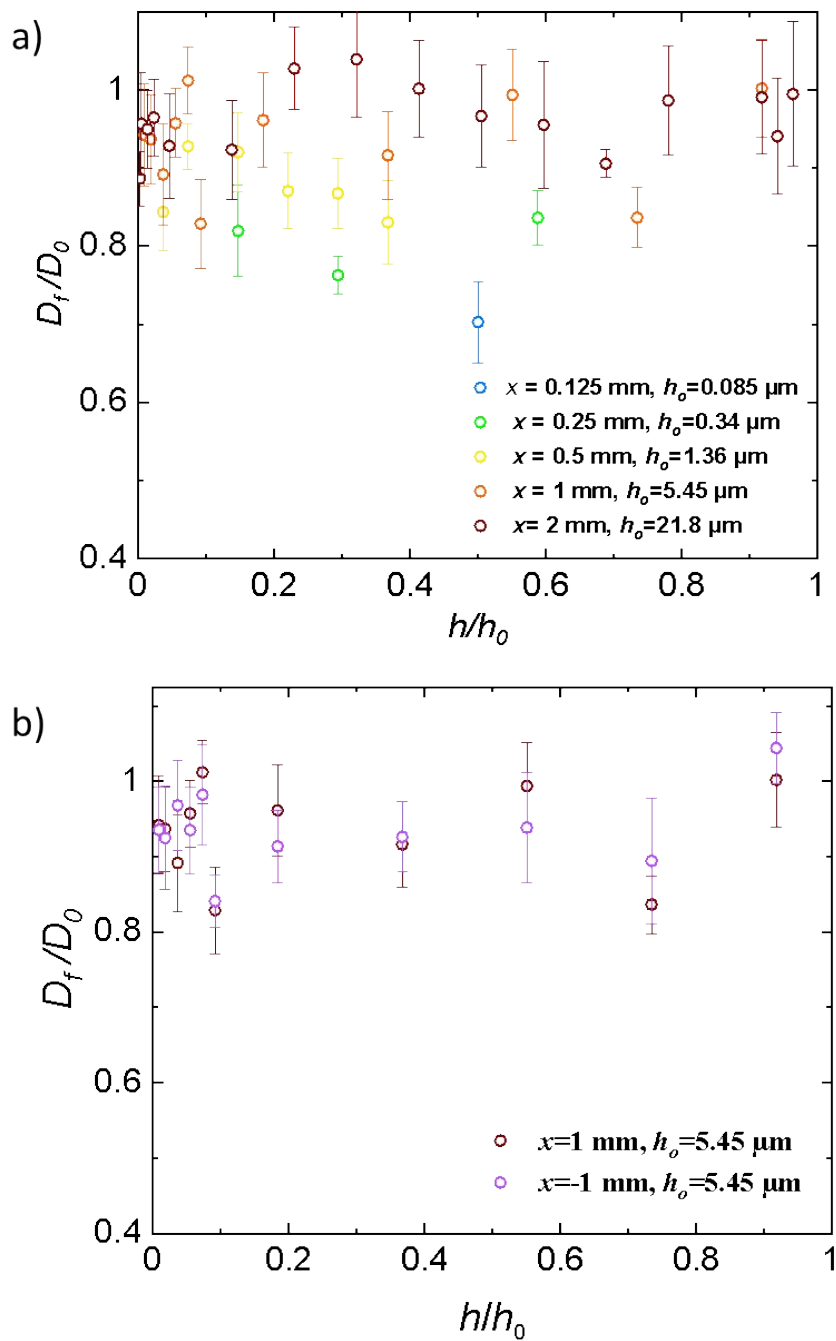


Figure S5 Relative diffusion coefficient as a function of height from the surface for $\phi=0.00005$. (a) At all measured radial positions. (b) At two symmetrical radial positions ($x = 1$ mm and -1 mm).

Confinement height measurement:

Total confinement heights in CLiC were measured using the dye technique. Samples were prepared using Alexa 488 dye diluted in 1X phosphate-buffered saline (PBS) at 0.05 and 0.5 mg/ml. To increase the area of view, a 10X objective was used for measuring micrographs shown in Figures S6 a&b. As defined in Eq. 3, the fluorescent intensity is directly proportional to the confinement height.

$$I(h_o) = ch_o\delta \quad (3)$$

Where, δ is the proportionality constant. To determine δ , the background intensity was first subtracted from the measured intensities so that only the dye emission signal is included in the calculations. $I(h_o)/h_o$ vs c relationship was then fitted with a linear profile at arbitrary radial position with known confinement height (Figure S6 c). The slope of this profile is δ . The results of the total confinement height as a function of radial position are shown in Figure S7. A good agreement between experimental and theoretical heights is achieved for the range of radial positions measured ($x = 0 - 0.6$ mm). Note that the theoretical heights were computed based on the

radial of curvature (R_c) as noted in the manuscript ($h_o = \frac{x^2}{2R_c}$).

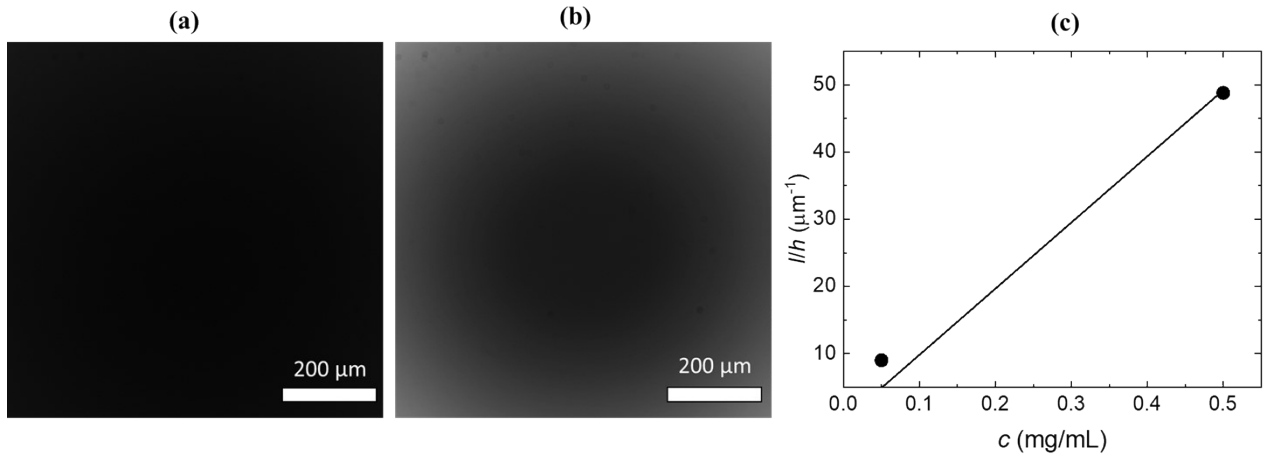


Figure S6 Typical dye intensity data measured in CliC using 10X objective. (a) $c=0.05$ mg/ml. (b) $c=0.5$ mg/ml. (c) Normalized intensity as a function bulk concentration. The linear line is a fit with a slope of $100 \text{ mL}/(\mu\text{m}^{-1}\text{mg})$.

Confinement interactions:

It has been shown before that surface interactions influence confinement. Notably, Malone et al.¹ took into account charge interactions in confinement by incorporating a Boltzmann factor that accounts for the near-wall particle-wall interaction energy:

$$\frac{D}{D_0} = \left(\frac{\mu_0}{\mu_a}\right) K(\phi) K_c(\lambda) \frac{2}{(1-\lambda)^2} \int_0^1 \exp\left(-\frac{E_{pw}(\beta,)}{k_b T}\right) \beta d\beta \quad (4)$$

where β is the normalized dimension within the channel, $2h/h_0$ and $E_{pw}(\beta,)$ is the energy between the particle and the wall, which can also be described in terms of Van der Waals and electrostatic interactions.

$$E_{pw}(\beta,) = U_{vdW}^{pw} + U_{el}^{pw} \quad (5)$$

$$U_{vdW}^{pw} = \frac{A}{6} \left(\ln \left(1 + \frac{2a}{\frac{h_0}{2} - h - a} \right) - \frac{\left(\frac{2a}{\frac{h_0}{2} - h - a} \right) \left(1 + \frac{a}{\frac{h_0}{2} - h - a} \right)}{1 + \frac{2a}{\frac{h_0}{2} - h - a}} \right) \quad (6)$$

$$U_{el}^{pw} = B \exp -\kappa \left(\frac{h_0}{2} - h - a \right) \quad (7)$$

$$B = 16 \epsilon a \left(\frac{k_b T}{e} \right)^2 \tanh \left(\frac{e \Psi_s^p}{4 k_b T} \right) \tanh \left(\frac{e \Psi_s^g}{4 k_b T} \right) \quad (8)$$

Where r is the interparticle distance, Ψ_s^p is the surface potential of the particles (~ -0.036 V),² Ψ_s^g is the surface potential of the glass (~ -0.05 V), κ is the inverse Debye screening length

($\sim I^{1/2}/0.304 \text{ nm}^{-1}$), I is the solution ionic strength, a is the particle radius, e is the electron

charge, A is the Hamaker constant between a particle and the wall ($\sim 3 \times 10^{-20}$ J), and ϵ is the dielectric permittivity of water.

The DLVO-type energy predicted from Eq. 5 is shown in Figure S6 as a function of salt concentration. When $h_0 = 85$ nm, the surface interactions are expected to influence particle dynamics. In fact, in low salt concentrations, numerical integration of Eqn.4 predicts that $\frac{D}{D_0}$ should be 500 times slower. Even when $h_0 = 360$ nm, the dynamics are expected to be ~ 7 times slower in deionized water, which is not observed in our experiments. This could be due to self-screening of the particles themselves, which increase the ionic strength of the solution, or due to more complicated effects like dielectric constant changes, and pH gradients, in confinement.³ In larger gaps, and higher salt concentrations, surface interactions do not influence dynamics in the CLiC geometry, especially in the middle of the channel. However, as the ionic strength of the solution increases, the repulsive surface interactions are screened. This results in a purely attractive surface for in higher ionic strengths, and could lead to more particle adsorption.

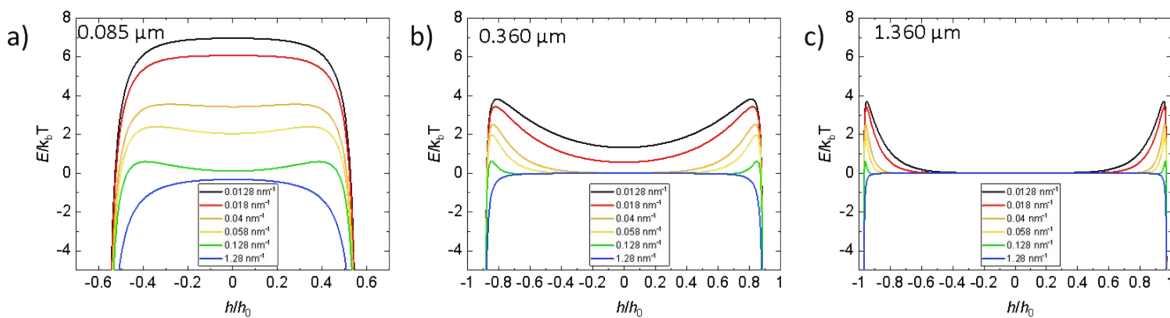


Figure S7. Surface energies as a function of confinement height. a) 0.085 μm b) 0.360 μm and c) 1.360 μm .

References

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- 3 L. Fumagalli, A. Esfandiar, R. Fabregas, S. Hu, P. Ares, A. Janardanan, Q. Yang, B. Radha, T. Taniguchi, K. Watanabe, G. Gomila, K. S. Novoselov and A. K. Geim, *Science* (80-.), 2018, **360**, 1339–1342.