In situ observation of colloidal monolayer nucleation driven by an alternating electric field

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Two- dimensional (2D) nucleation theories

$$\Delta G_{\mathrm{crit}} = \frac{\pi \Omega \gamma^2}{\Delta \mu} \quad (1)$$

ΔG_{crit} : *nucleation barrier*

$$r_c = \frac{\Omega \gamma}{\Delta \mu} \quad (2)$$

Growth becomes energetically favourable only when the crystallites reach a critical size.

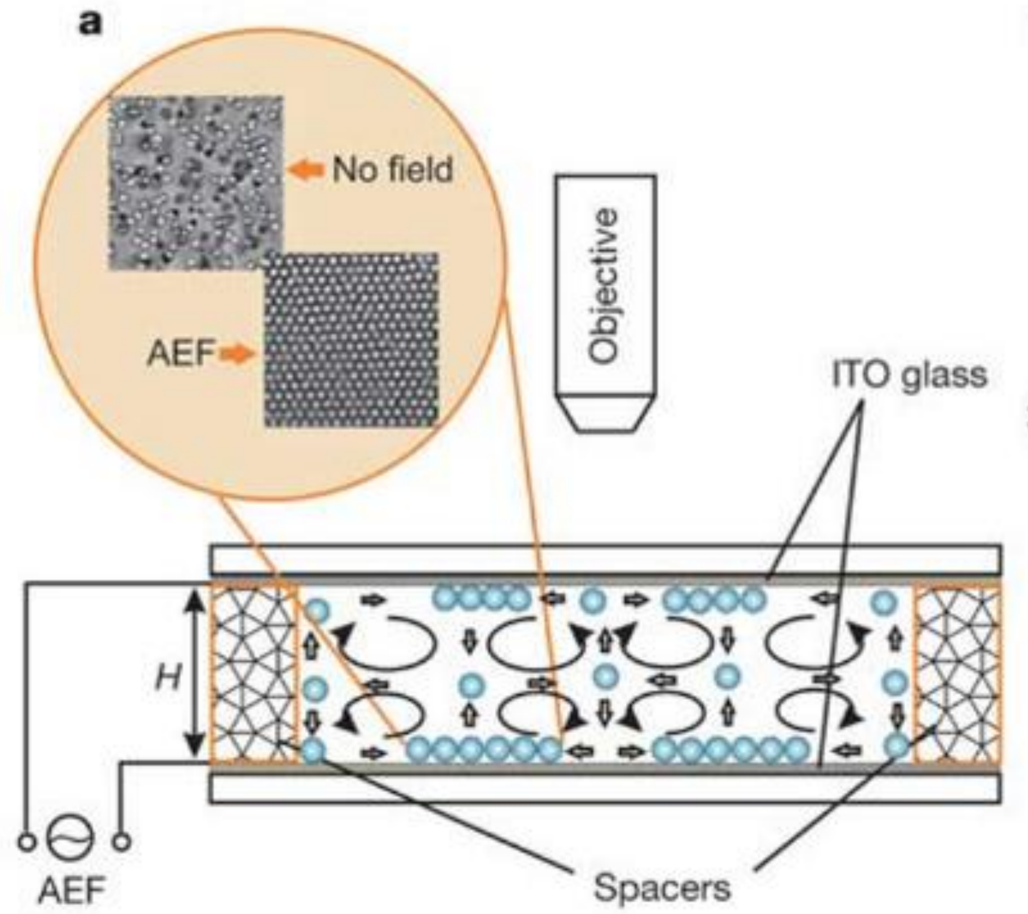
$\Delta\mu$: the difference in chemical potential between the growth units in the crystal and the liquid phase
r_c : radius of critical circular nucleus
γ : the crystal–liquid interfacial edge free energy (or line tension)
Ω : the area per structural unit.

?

Can we design an experiment to validate this theory quantitatively?
How can we get parameters, $\Delta\mu$, r_c

In situ observation of colloidal monolayer nucleation

Colloidal suspensions have been used as experimental model systems for the study of crystal nucleation and structural phase transitions, as their crystallization phase diagram is analogous to that of atomic and molecular systems.



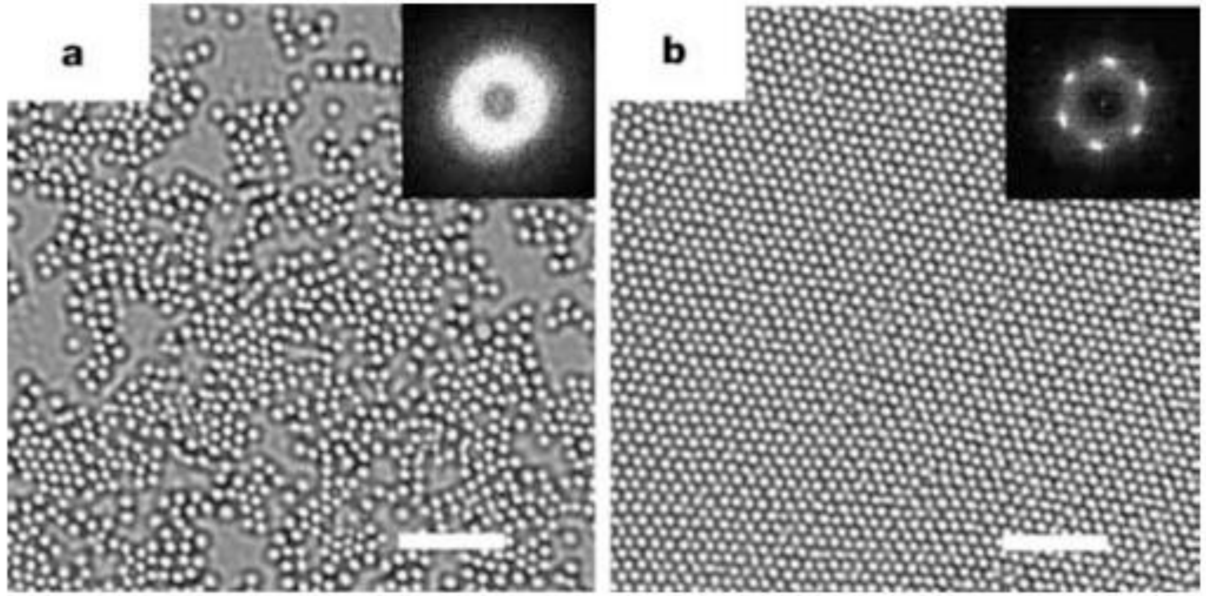
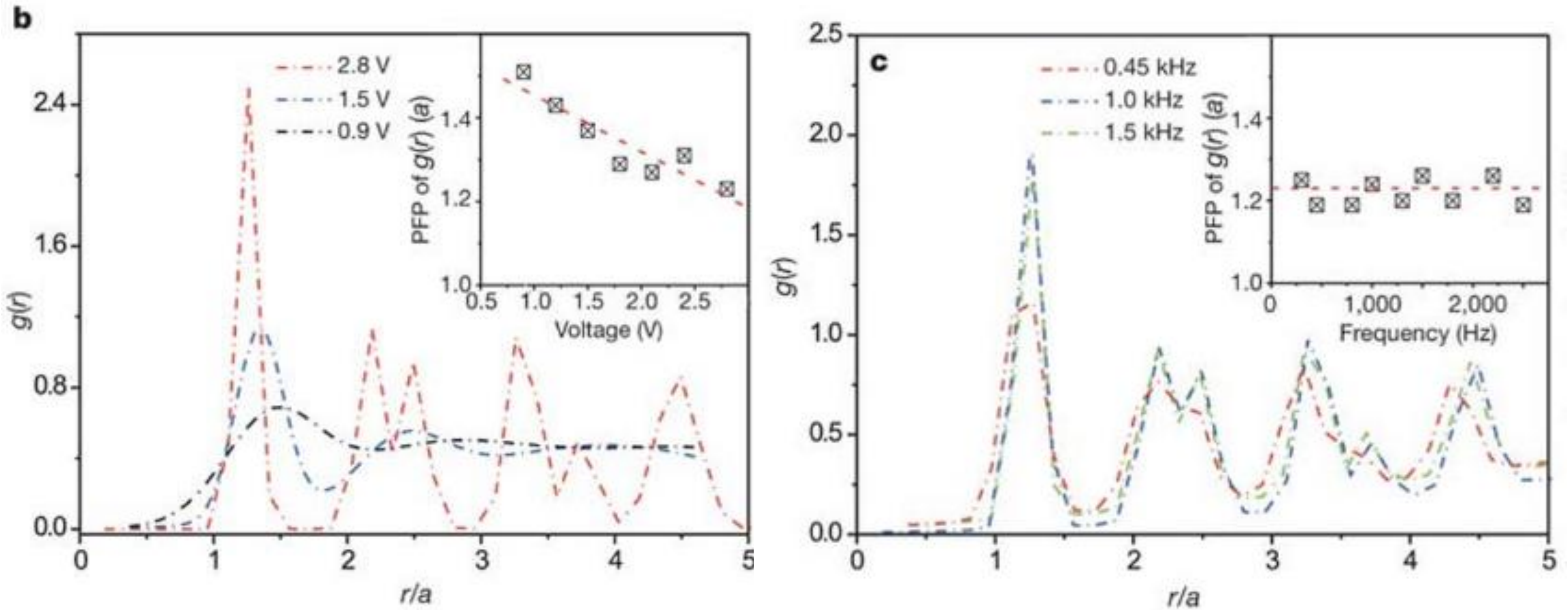


Figure 4 Comparison of the colloidal assemblies obtained under constant electric field and under an AEF. **a**, Constant electric field at 3.2 V. The fast Fourier transform (FFT) in the inset at upper right shows the diffraction ring. **b**, AEF at 2.4 V, 600 Hz. The FFT in the inset at upper right shows the uninterrupted six-fold symmetry of the hexatic phase. Scale bars, 10 μm.

The effect of the voltage and frequency on the colloidal crystal structure

The pair correlation function (PCF): g(r)



1. Vpp (or the field strength E) changes the interaction between neighboring particles
2. the frequency will not affect the interparticle interaction

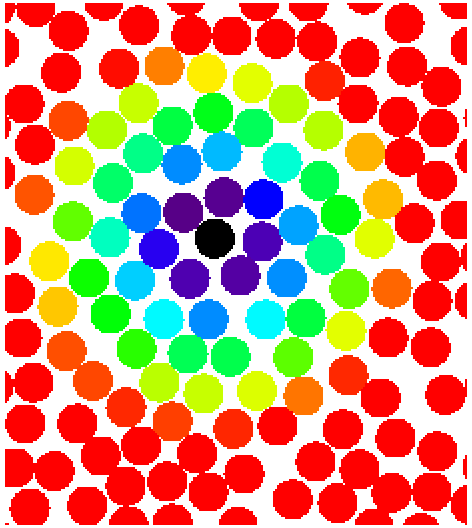
The pair correlation function

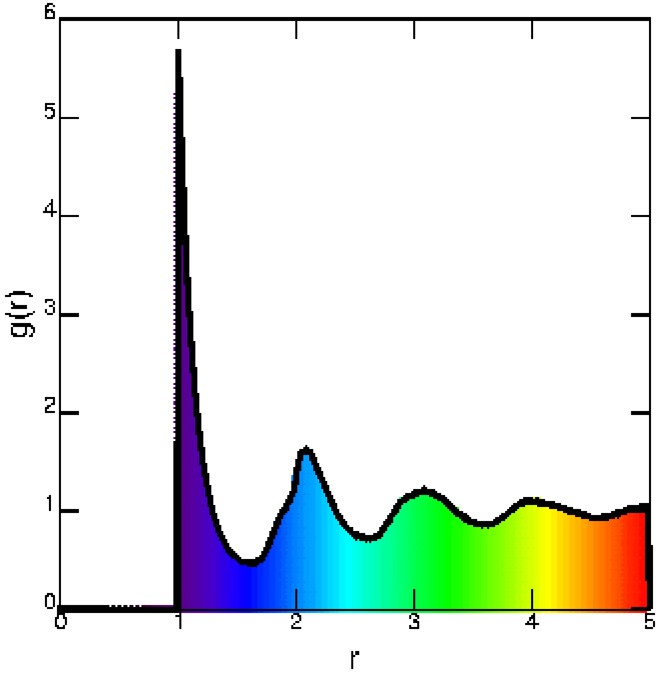
$U_{eff}(r)$ is effective pair-wise interaction potential

$$g(r) = \exp\left(-\frac{U_{\rm eff}(r)}{k_{\rm B}T}\right)$$

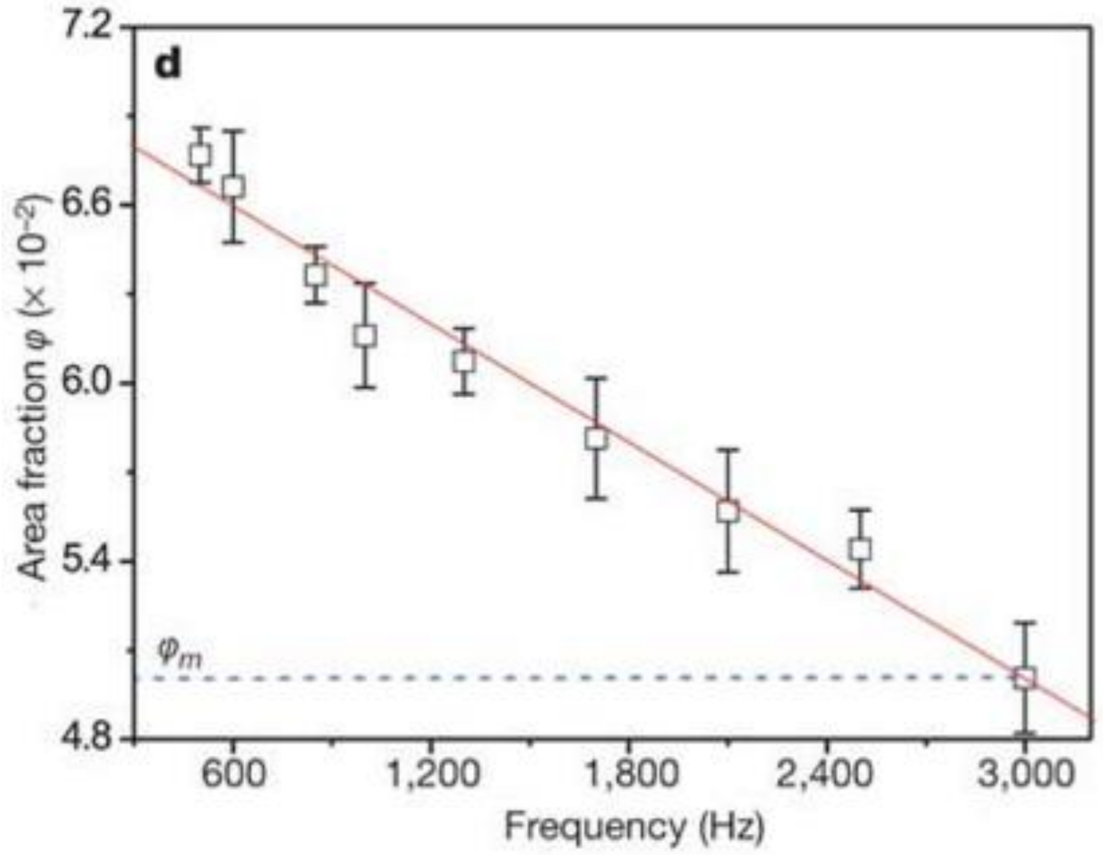
$$\frac{dn(\mathbf{r})}{d^3r} = \langle \textstyle\sum_{i\neq 0} \delta(\mathbf{r}-\mathbf{r}_i)\rangle,$$

$$g(\mathbf{r}) = \frac{1}{\rho}\langle\sum_{i\neq 0}\delta(\mathbf{r}-\mathbf{r}_i)\rangle = V\frac{N-1}{N}\langle\delta(\mathbf{r}-\mathbf{r}_1)\rangle$$





Calculate the driving force $\Delta\mu$ and r_c



$$\Delta\mu = k_B T \ln(1+\sigma) \qquad (3)$$

$$\sigma = \frac{\varphi - \varphi_m}{\varphi_m} \qquad (4)$$

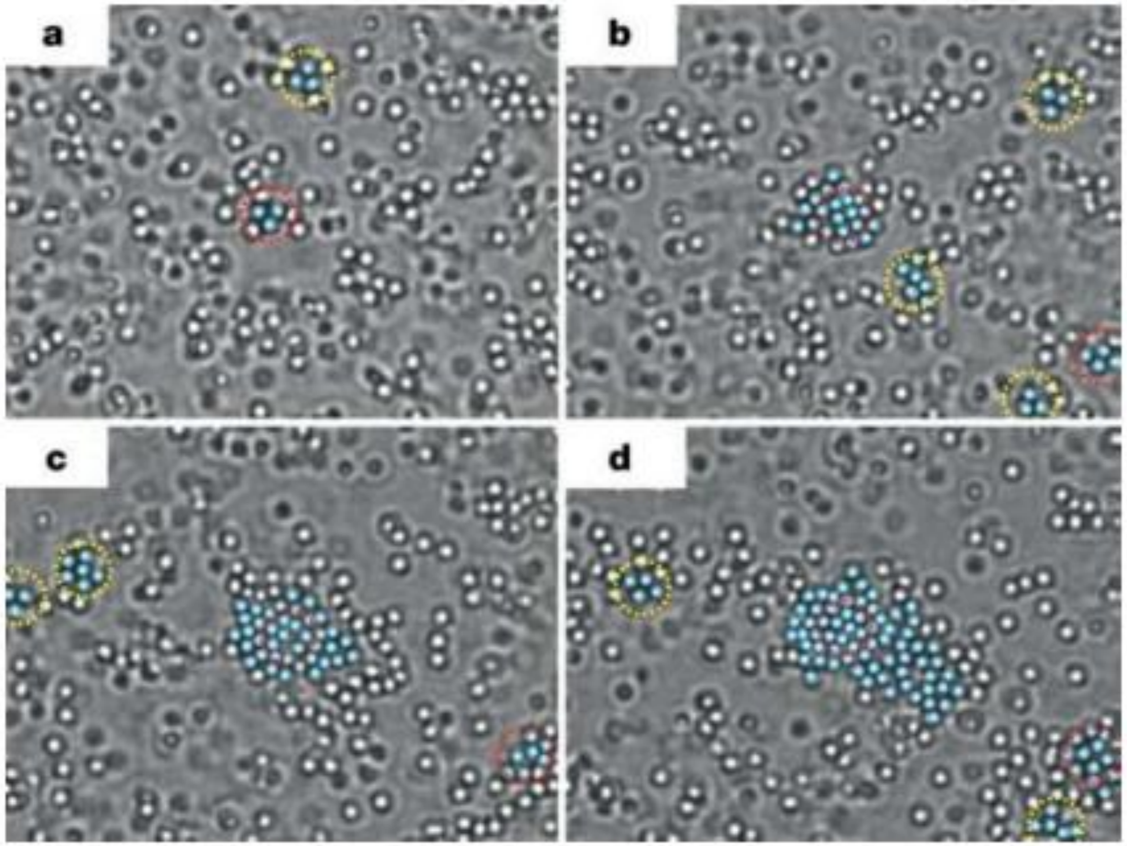
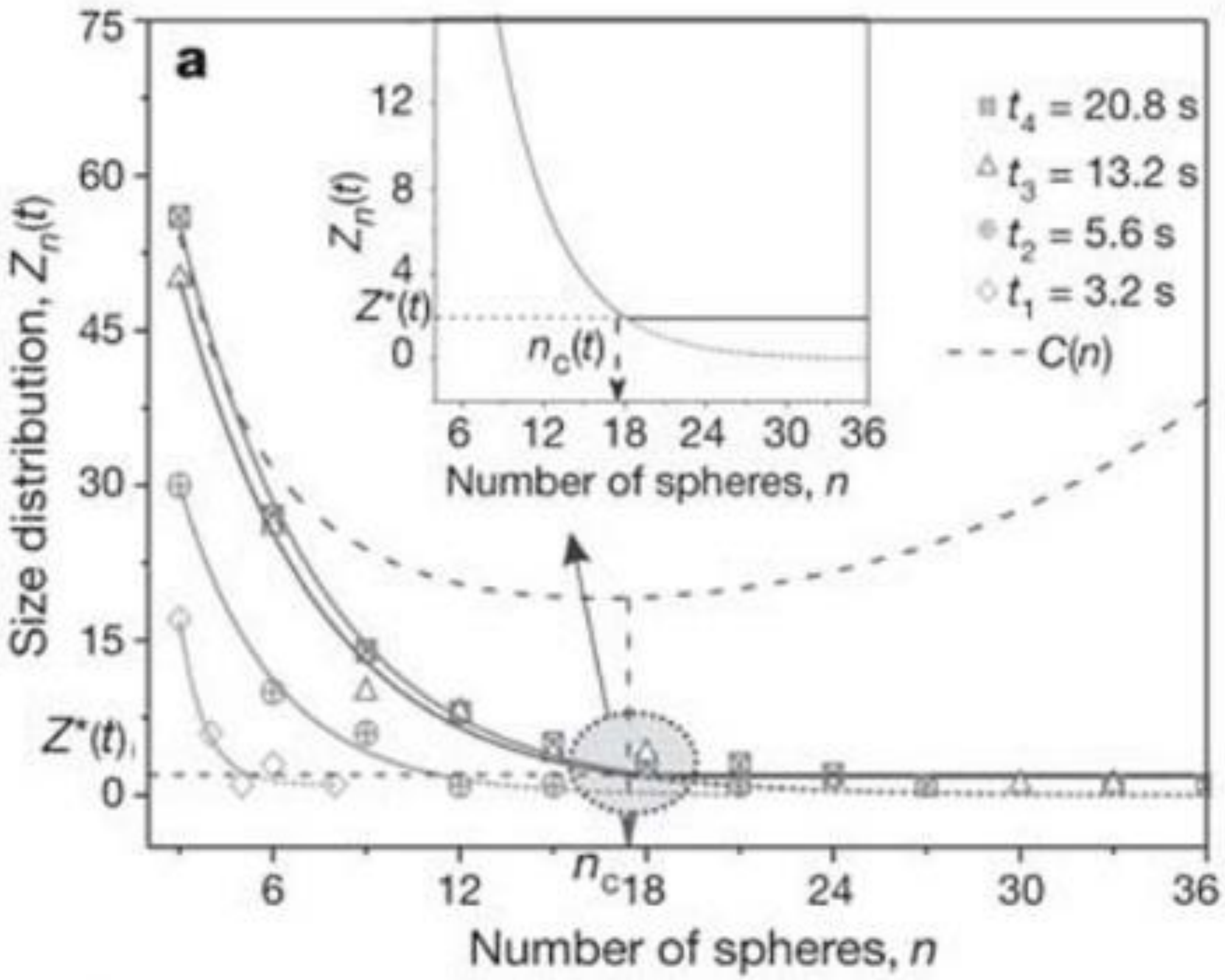
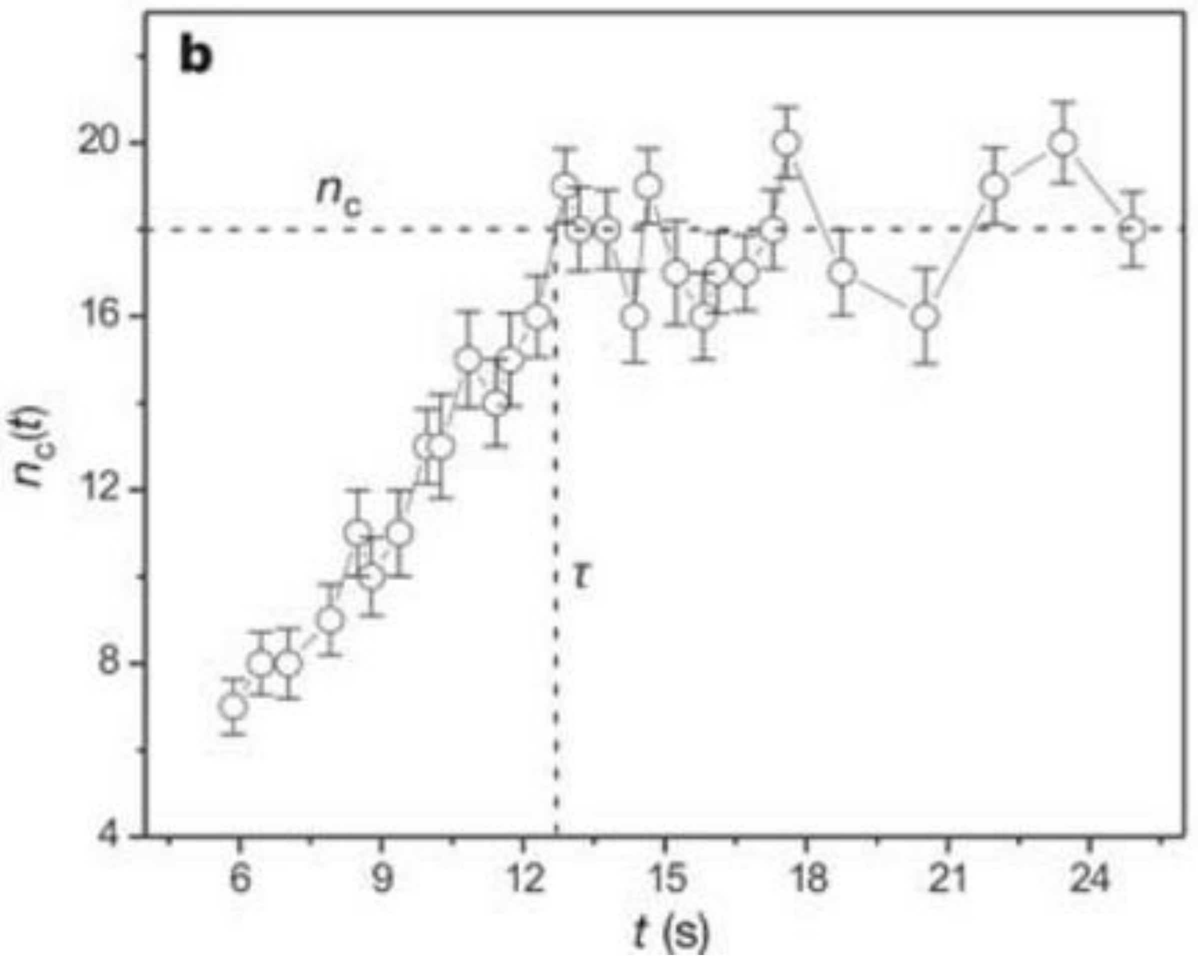


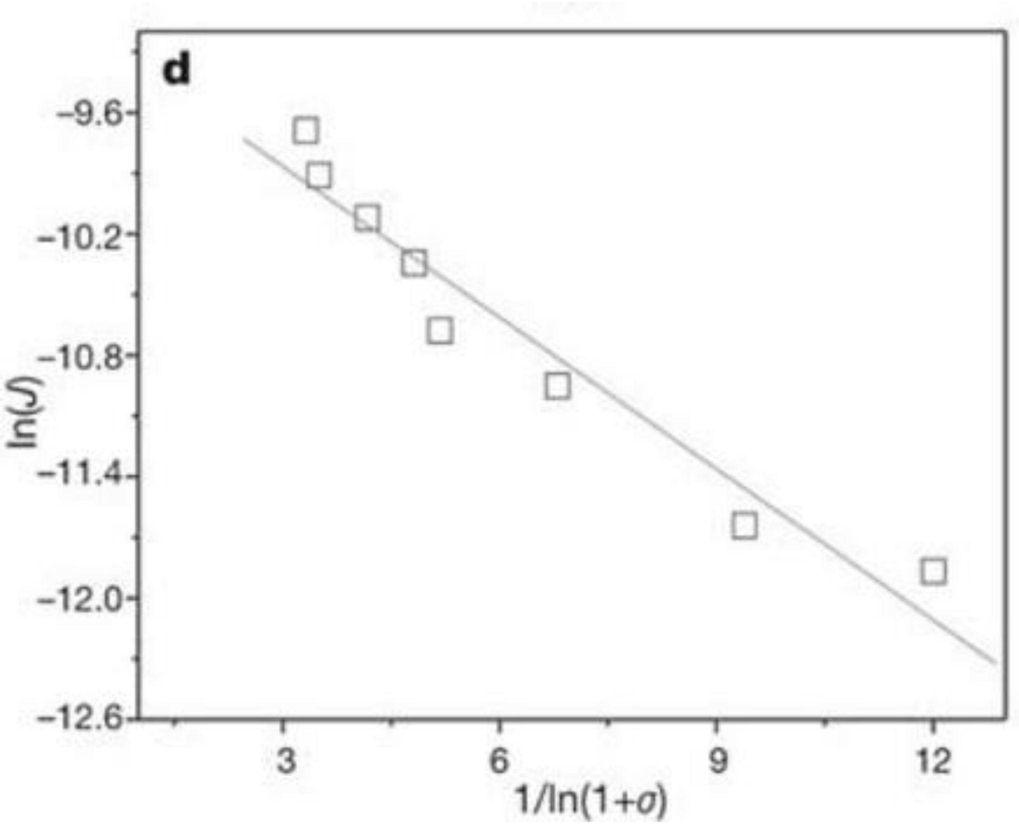
Figure 2 Snapshots of the pre-nucleation process at multiples of $t_0 = 0.294$ s, where t_0 is the timing interval of the images. The radius of the red and yellow circles equals the critical radius r_c at the given supersaturation ($V_{pp} = 2.4$ V, $f = 600$ Hz). The bright dots correspond to the well-focused spheres that are confined on the bottom of the electrodes. The dark dots correspond to the ill-focused spheres, which are suspended in the bulk solution. $t = 14t_0$ (**a**), $34t_0$ (**b**), $54t_0$ (**c**), and $74t_0$ (**d**).

Statistical measurements of parameters of nucleation kinetics





Statistical measurements of parameters of nucleation kinetics

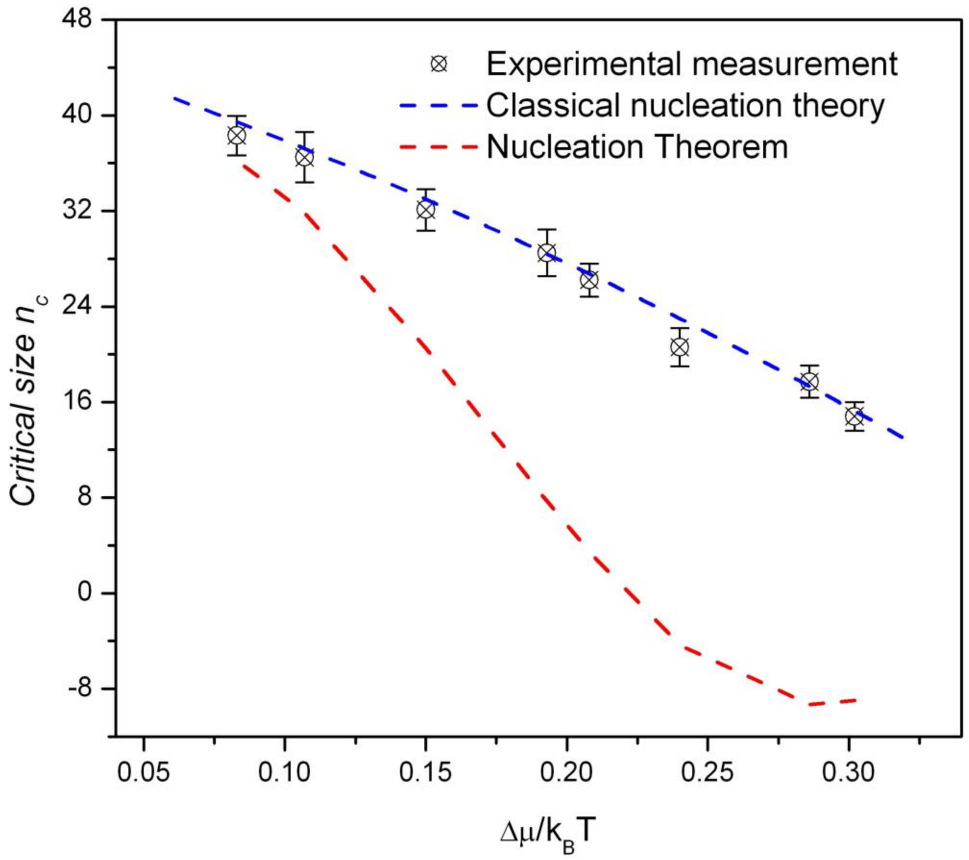


$$J = C\left\{\frac{2D_s n_1^2}{\pi}\left[\frac{\Omega \ln(1+\sigma)}{a}\right]^{1/2} \exp\left(-\frac{\pi \Omega \gamma^2}{(k_B T)^2 \ln(1+\sigma)}\right)\right\} \quad (5)$$

Conclusions

Table The measured kinetics parameters of nucleation of colloidal monolayer at the various values of the driving force.

$f\,(Hz)$	φ (10^{-2})	$\Delta\mu\,(k_BT)$	n_c*	$r_c\,(a)$	$\gamma\,(k_BT/a)$	$\Delta G_{crit}\,(k_BT)$
500	6.77	0.302	14.8±1.19	1.92	0.442	4.47
600	6.66	0.286	17.7±1.35	2.10	0.458	5.06
850	6.36	0.240	20.6±1.60	2.27	0.416	4.94
1000	6.16	0.208	26.2±1.38	2.56	0.406	5.41
1300	6.07	0.193	28.5±1.94	2.67	0.393	5.50
1700	5.74	0.150	32.1±1.73	2.83	0.324	4.82



Experiments provide crucial experimental verification for different models and theories. The above data are in very good agreement with classical 2D nucleation.