Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Can the pathway of stepwise nucleation be predicted and controlled?

Tian Hui Zhang,*[a] Zhi Chao Zhang[a], Jing Sheng Cao[a], Xiang Yang Liu[b]

[a] *Center for Soft Condensed Matter Physics and Interdisciplinary Research & School of Physical Science and Technology, Soochow University, Suzhou, P. R. China.*

[2] *Department of Physics, FOS, NUS, Singapore*

Supporting information

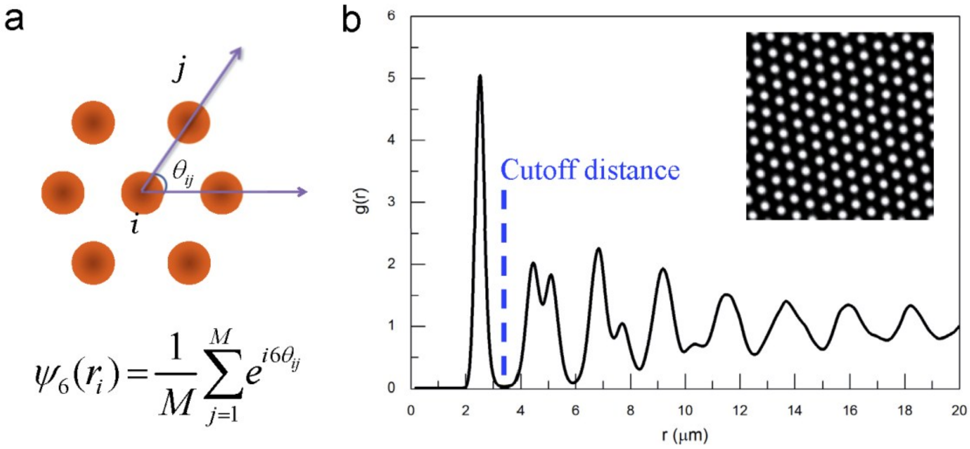

Figure S1 a, Definition of the six-fold bond-orientational order parameter ψ_6. **b**, Cutoff distance and pair distribution function foe 2D hexagonal crystals. The mid position in the first valley is used as the cutoff distance to identify the nearest neighbors.

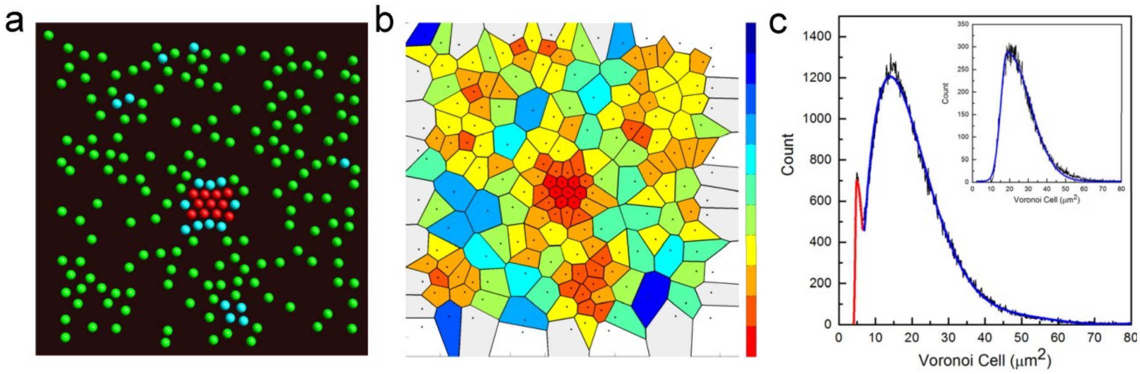

Figure S2 Voronoi area. **a**, A crystal nucleus and the surrounding liquid phase. **b**, Voronoi tessellation divides the plane into nonoverlapping polygons. With the area S of the polygons, the local number density (concentration) C can be estimated from $C = 1/S$. In the colored Voronoi tessellation, the highest density (red) rises from the crystalline region. **c**, The distribution of the area in the coexisting state exhibits two peaks. The left peak (red solid line) arises from the crystalline region and the right peak (blue solid line) represents the average area in the liquid phase. The inset represents the distribution in the liquid phase alone.

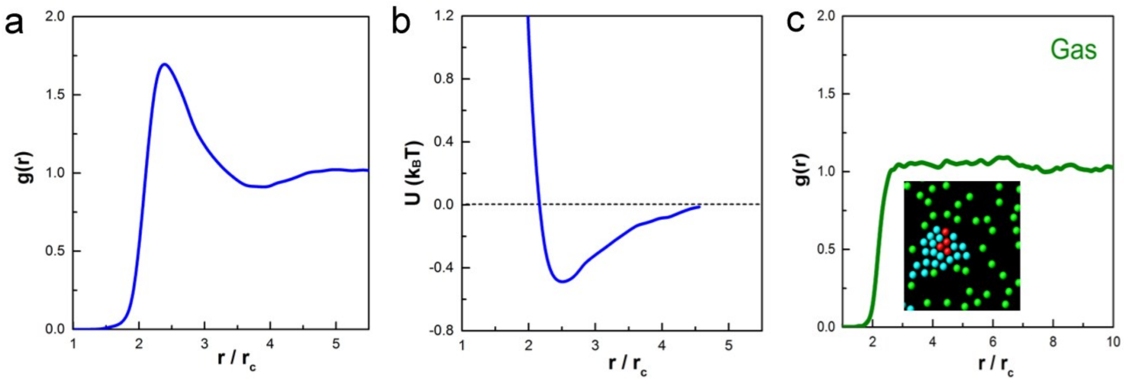

Figure S3 Pair correlation and pair potential. With a pair distribution function, the pair attraction may be obtained from the Ornstein-Zernike integral equation.[1] This approach can offer a good estimation of the pair attraction in the dilute phase because the many-body effect is not significant. **a**, The pair distribution function arising from the crystal nuclei observed at f = 3.0 kHz. **b**, Pair attraction in crystal nuclei at f = 3.0 kHz. Although under the high-density condition, such as in the crystal nuclei, the estimation of pair attraction based on Ornstein-Zernike integral equation is not accurate anymore due to the many-body effect, it can serve as a rough estimation. Here, it shows that the interaction between (red) particles in the nuclei is robust. **c**, In the final stable crystal-gas coexisting state, the pair distribution function in the dilute phase exhibits no peaks, suggesting that there is no considerable space correlation between the gas (green) particles and that the interaction between gas particles is negligible. Green spheres: particles in the gas phase. Blue spheres: liquid-like particles in the nuclei. Red spheres: crystal-like particles in the nuclei.

Video 1 Crystal nuclei in equilibrium with the dilute gas

This video is played in real time at 17 frames per second. In the movie, the red particle detaches from the nucleus while the green particle incorporates into the nucleus. This video reveals that, in the final equilibrium state of nucleation, the crystal nuclei are in dynamic equilibrium with the surrounding dilute phase: nuclei exchange particles with the dilute gas phase from time to time.

References

[1] Y. Han, D. G. Grier, *Phys. Rev. Lett.* **2003**, *91*, 038302.