Supplementary information for
"Density dependence of orientational order in one-patch particles"

Yasutaka Iwashita,[*] **and Yasuyuki Kimura**

Department of Physics, Kyushu University, 819-0395 Fukuoka, Japan
E-mail: iwashita@phys.kyushu-u.ac.jp
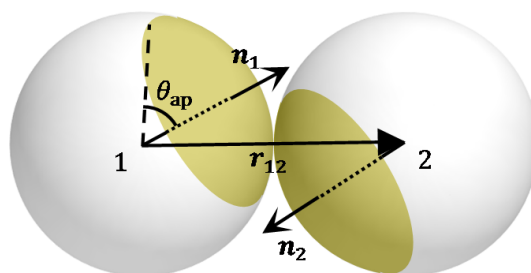
1 Simulation methods

Fig. A A schematic drawing of neighbouring one-patch particles.

The Kern-Frenkel model is used as the pairwise interaction between one-patch particles.[1] The pair potential between particles 1 and 2, u_{12}, is written as follows :

$$u_{12}(\boldsymbol{r}_{12},\boldsymbol{n}_1,\boldsymbol{n}_2) = \begin{cases} \infty & \text{for } 0 < r_{12} \leq d \\ -\varepsilon \cdot f(\boldsymbol{r}_{12},\boldsymbol{n}_1,\boldsymbol{n}_2) & \text{for } d < r_{12} < d+\delta \\ 0 & \text{for } r_{12} \geq d+\delta \end{cases} \quad (1)$$

$$f(\boldsymbol{r}_{12},\boldsymbol{n}_1,\boldsymbol{n}_2) = \begin{cases} 1 & \text{if } \boldsymbol{n}_1 \cdot \hat{\boldsymbol{r}}_{12} \geq \cos\theta_{\text{ap}} \\ & \text{and } \boldsymbol{n}_2 \cdot \hat{\boldsymbol{r}}_{12} \leq -\cos\theta_{\text{ap}} \\ 0 & \text{otherwise} \end{cases} \quad (2)$$

d is the particle diameter, $\hat{\boldsymbol{r}}_{12} = \boldsymbol{r}_{12}/r_{12}$ and $\boldsymbol{r}_{12}$ is the vector from the centre of particle 1 to that of particle 2, ε is the depth of the inter-patch attractive potential and $\delta = 0.01d$ is the range of the square-well potential. $\boldsymbol{n}_i$ is a unit vector determining the position of the patch centre on particle i.

In a simulation step, a random translational and rotational move is attempted for a randomly selected particle, and the moves are judged independently. The selection is done N times in a step, where $N =$

2048 is the number of particles in a system. The length of a rotational step is less than $\pi/30$. The range of a translational step depends on the packing density of a system, calculated from the lattice constant of particle arrangement l before the configuration is randomized to prepare the initial state. The length of a translational step is less than $0.01d$ when $l - d \leq 0.01d$, otherwise less than $l - d$, taking the rate of acceptance of a step into account. The number of total simulation steps is 10^7. Four independent simulation runs were carried out for each parameter set and the results were averaged to give final statistics, Fig. 9.
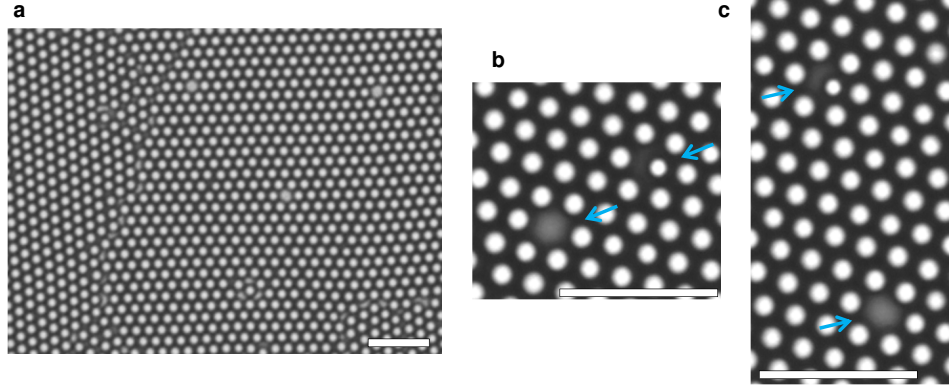
2 Evaluation of particle packing

Fig. B Optical microscopy images of a close packed monolayer of bare silica particles for $d = 2.04$ μm. A hexagonal arrangement is clearly observed in (a). In the magnified images in (b) and (c), voids and particles smaller than the surrounding ones are indicated with arrows. All scale bars are 10 μm.

We measured the centre-to-centre distance between nearest neighbours, r, in typical ordered states in a hexagonal monolayer to compare local packing conditions for particles. Local density in a pattern can be estimated from r, such as $(\pi/2\sqrt{3})(d/r)^2$ for area fraction. However, this is not directly related to the total density or fraction of particles in a system. An experimentally-realized close packed crystalline structure of monodisperse hard spheres usually contains defects such as voids and grain boundaries, which reduce the density and fraction (Fig. B). In addition, precisely estimating the total density or fraction is difficult in some patterns because single particles are not clearly resolved in a microscopy image (see e.g. Fig. 6). How to determine r is thus dependent on the appearance of a pattern: measuring directly from an image, estimating from the Fourier transformation of a pattern or from the number of particles in an image.

2.1 Close packed monolayer of bare silica particles

The particles, used also for preparing the one-patch particles (see Sec. 2), formed a monolayer at the air-water interface, then the monolayer was transferred onto a glass substrate and dried (Fig. B). On drying, the capillary interaction by water induces a strong attraction between particles, and thus the particles are considered to be almost close packed. The distance $r_{\mathrm{si}} = 2.07$ μm in a monodomain for $d = 2.04$ μm. The difference between r_{si} and d is probably due to the size dispersion, $\simeq 3\%$. A smaller particle than average can be in a monolayer without disturbing the lattice (Fig. B (b) and (c)); a larger particle extends it.

2.2 Tightly packed monolayer of one-patch particles (Figs. 4 and 6)

The pattern in a P_Δ state is locally anisotropic, and thus the characteristic distance is also anisotropic. The distance parallel to a linear domain $r_{P_\Delta}^{\parallel} = 2.07 - 2.08$ μm, whereas the characteristic distance between linear domains, $\lambda_1 = 3.62$ μm in Sec. 3.1.1, corresponds to $r_{P_\Delta}^{\perp} = 2.09$ μm. In the H state, $r_H = 2.06 - 2.08$ μm. The value of r is slightly inhomogeneous in a pattern as expected from the existence of voids, grain boundaries and other types of defects. In addition, the fact that r_H can be smaller than r_{si} is acceptable because a larger particle than average cannot intrude into the space when its d_s is larger than the confinement thickness L.

2.3 Closely packed monolayer of thermally rotatable one-patch particles

In this packing regime, the characteristic distance is typically a few % larger than that under tight packing. In a ZS state, see e.g. Fig. 6c1, r measured parallel to the linear domains $r_{ZS}^{\parallel} = 2.09 - 2.10$ μm, and the characteristic distance between linear domains corresponds to $r_{ZS}^{\perp} = 2.11 - 2.13$ μm. In a Tr state, see e.g. Fig. 6c3, $r_{Tr} = 2.12 - 2.13$ μm.

3 Supplementary figures

References

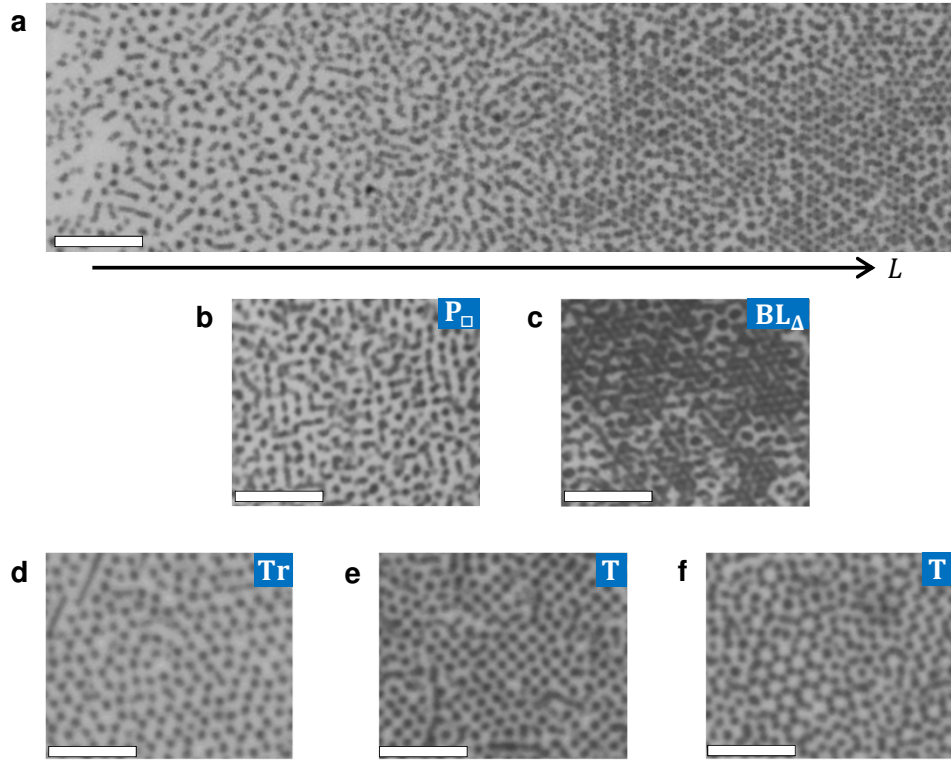1 N. Kern and D. Frenkel, *J. Chem. Phys.*, 2003, **118**, 9882–9889.

Fig. C Orientational ordering observed for $d = 1.0\ \mu$m and $\theta_{ap} = 62°$. (a - c) are the structures observed under tight packing. (a) shows the confinement thickness dependence in a monolayer, (b) shows the order with a confinement corresponding to 2□, and (c) to 2Δ. (d - f) are structures seen when the particles are closely packed and able to rotate thermally. (d) is 1Δ, (e) is 2□ and (f) is 2Δ. All scale bars are 10 μm.