

Supplemental Materials

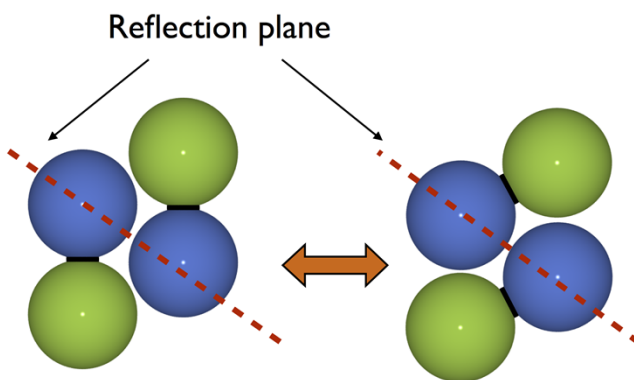
Simulation Methodology

The phase behavior of dimers as a function of gap height H was determined using Monte Carlo simulations in the isothermal-isobaric (NP,T) and isothermal-isostress ($N\sigma,T$) ensembles, where the number of particles N , the temperature T , and the lateral pressure P_t (or lateral stress σ_t) were kept constant. The latter ensemble is necessary in order to avoid possible stress in solids induced by the use of orthorhombic boxes.

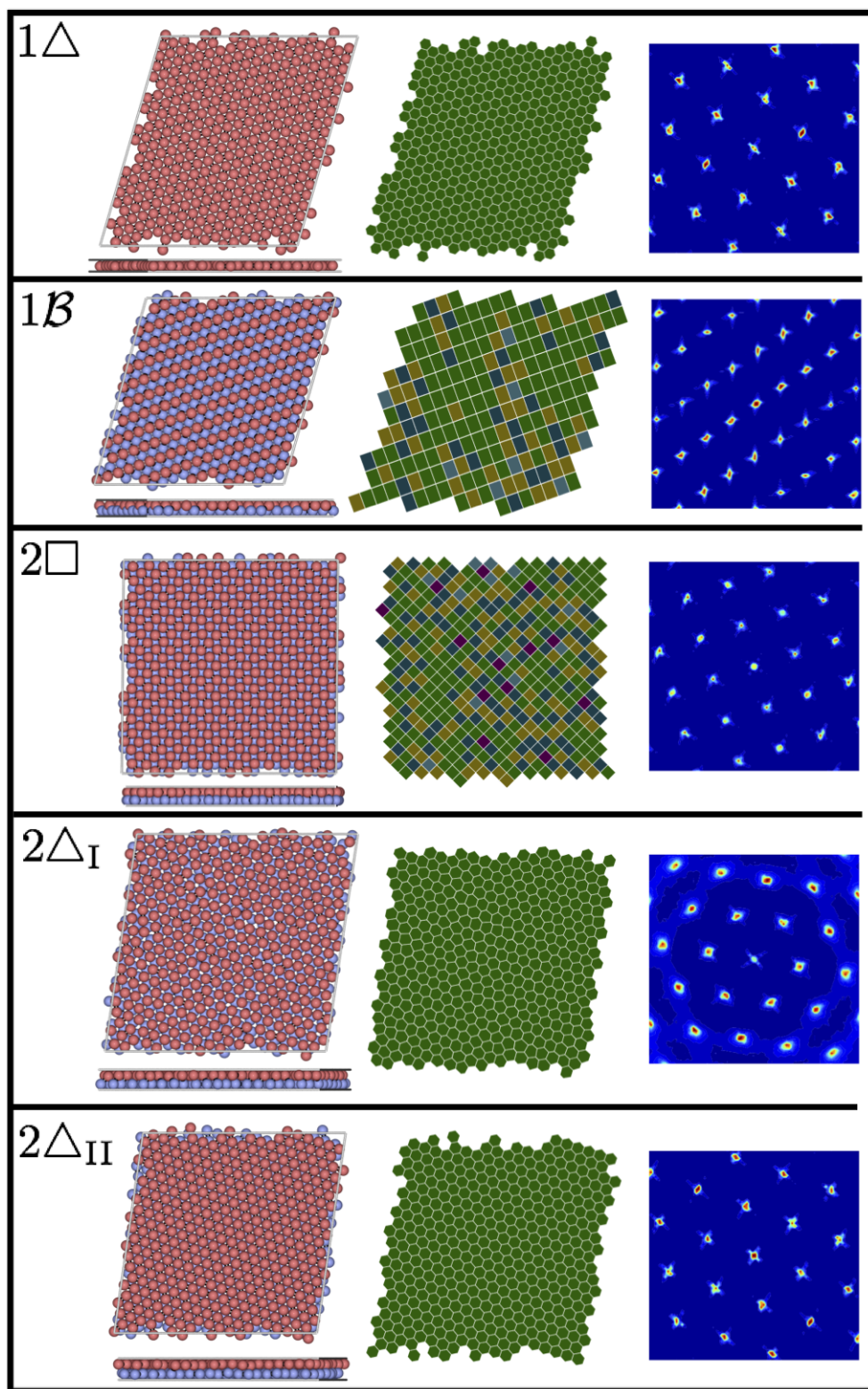
Standard Monte Carlo moves at high pressure undoubtedly will prevent the orientation of the particles to be sampled adequately. For this reason, apart from the standard MC moves, a cluster move similar to the one reported in references^{1,2} is also implemented. Only clusters involving pairs of dimers are used in this work, and the move is illustrated schematically in Supplemental Figure 1. This move has to be fully reversible, and hence the acceptance probability is modified accordingly. The cluster move is implemented as follows:

- A particle k is randomly selected.
- The number of two-particle clusters $N_{c,i}$ that the particle k can form with neighbor particles is counted. A pair of particles are said to form a cluster if the distance between the centers of masses of the dumbbells is less than 1.05σ . If $N_{c,i} \neq 0$ then proceed to the next step, otherwise reject the move.
- Select one of the $N_{c,i}$ pairs at random, and perform the reflection operation using the plane that is parallel to the inter-site vector between the centers of the two farthest spherical sites in the cluster, and is the most orthogonal with respect to the inter-site vector between the center of the two closest spherical sites (see Fig. 1).
- If after the reflection operation no overlaps are found, count the number of clusters of two particles $N_{c,j}$ that the particle k can form in the new configuration. If overlaps are found the move is automatically rejected.
- Finally, accept the move with probability $P_{acc}(i \rightarrow j) = \min(1, N_{c,i}/N_{c,j})$

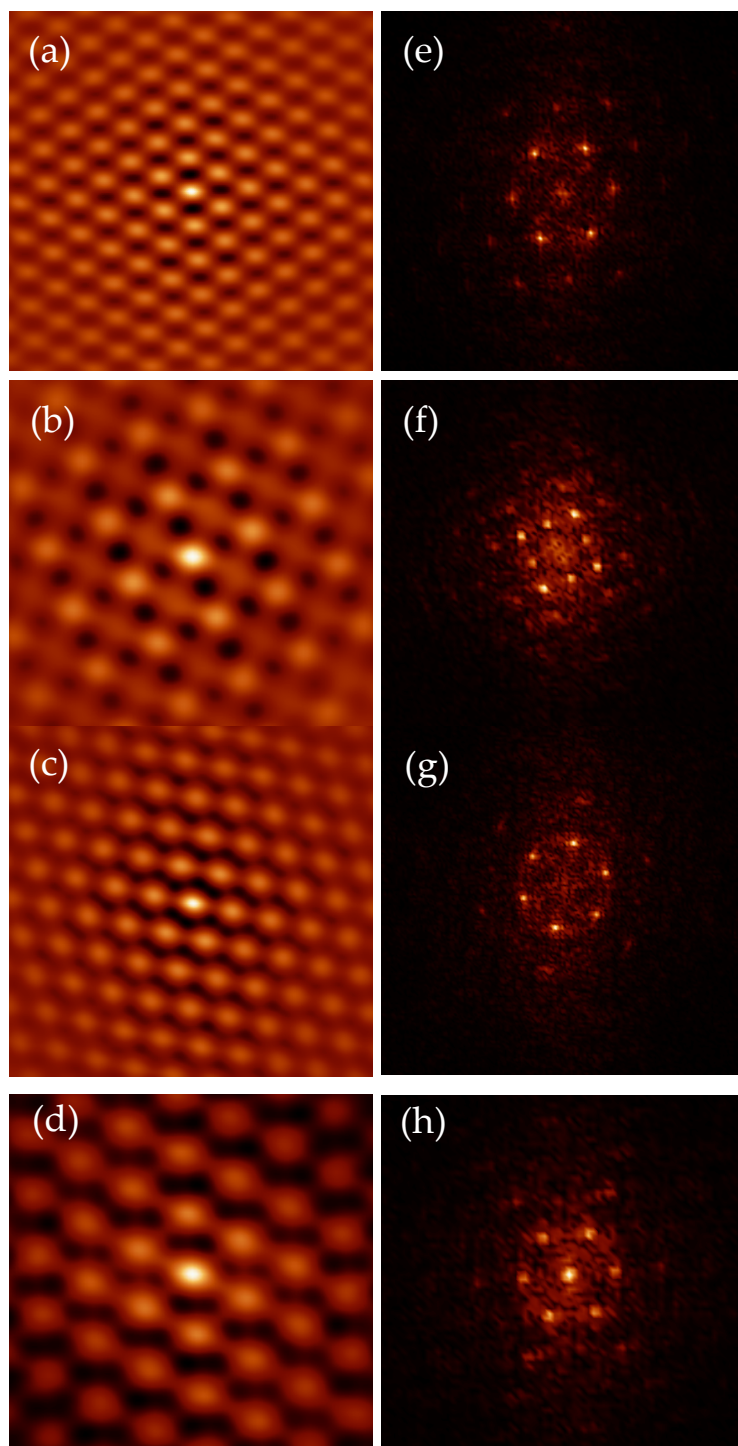
During the simulations, N cluster moves are attempted every 20 MC standard cycles. It was observed that these cluster moves allowed a fast sampling of multiple bond orientations of the dimers. This demonstrates the importance of implementing such moves for a proper configurational sampling and equilibration of the dimer structures (even with a low frequency of attempts).



Supplemental Figure 1. Scheme of cluster move to sample efficiently different configurations of the bonds for simulated crystal structures.



Supplemental Figure 2. Representative configurations, Voronoi diagrams, and structure factors in the x - y plane for the stable phases observed in the phase diagram of hard dimers obtained using MC simulations. From top to bottom, the structures corresponds to (a) hexagonal monolayer (1Δ), (b) buckled state ($1B$), (c) bilayer square $2\square$, (d) bilayer hexagonal type I ($2\Delta_I$), (e) bilayer hexagonal type II ($2\Delta_{II}$). Voronoi constructions and structure factors were calculated using positions of particles in a single layer.



Supplemental Figure 3. Autocorrelation functions (2D positional correlations) and fast Fourier transforms highlight the lobe based symmetry of the experimental phases, (a,e) hexagonal monolayer (1Δ), (b,f) bilayer square $2\Box$, (c,g) bilayer hexagonal type I ($2\Delta_I$), (e,h) bilayer hexagonal type II ($2\Delta_{II}$). The image analysis was done within grains from Figure 1 (i.e., confocal images) in the main text.

Supplemental Table 1. Packing density of experimental phases

| Phase | H* | ϕ |
|--------------------------|-----|--------|
| 1 Δ | 1.1 | 0.44 |
| 1B | 1.6 | 0.37 |
| 2 \square | 1.8 | 0.48 |
| 2 Δ _I | 1.9 | 0.54 |
| 2 Δ _{II} | 2.2 | 0.47 |

REFERENCES

1. K. W. Wojciechowski, D. Frenkel and A. C. Branka, Nonperiodic solid-phase in a 2-dimensional hard-dimer system. *Phys Rev Lett.*, 1991, **66**, 3168-3171.
2. M. Marechal and M. Dijkstra, Stability of orientationally disordered crystal structures of colloidal hard dumbbells. *Phys Rev E*, 2008, **77**.