Supplementary Information for

Phase behavior of polyhedral nanoparticles in parallel plate confinement

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In this section we provide order parameter plots associated with the phase behavior described in the main text. Given the large number of H* and pressure conditions explored in the simulations, only representative cases are presented. In the plots to follow, the order parameters used are selected from those defined in Sec. 2.1 of the main text and the symbols P_{41} and P_{42} are used to denote the P_4 order parameter values associated with the two largest and most orthogonal directors[1].

I. CUBE

As discussed in the main text, we did not observe cubatic mesophase as seen in the 3D case[1, 2]. However, for certain H* values (particularly, those close to H*=1), we see small regions with tetratic-like order. These regions are characterized by significant particle orientational order and intermediate four-fold bond-orientational order. As an example, we show plots for H*=1.1 and H*=1.9 (see Figures S1 and S2)
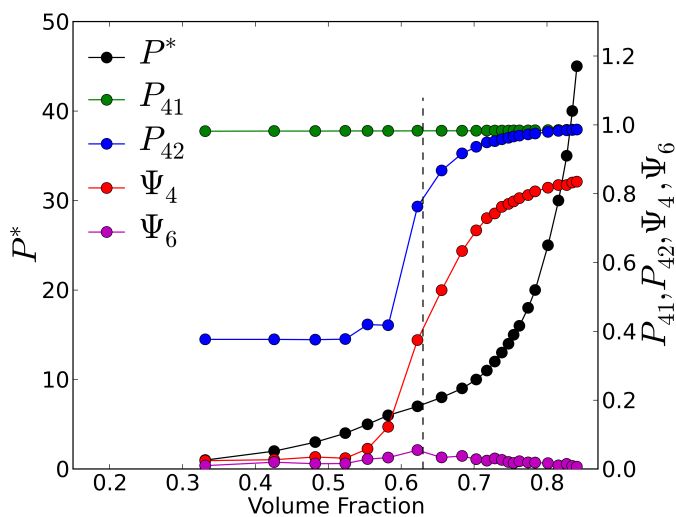

FIG. S1: Equation of state and concentration dependence of order parameters P_{41}, P_{42}, Ψ_4 and Ψ_6 for cubes at H* = 1.1. All order parameters are scaled so that they have a maximum value of 1.0. The region between $\phi = 0.58$ to 0.64 has significant particle orientational order and intermediate four-fold bond-orientational order. Dotted line indicates the transition between distinct phases as identified for the phase diagram.

II. TC4

The equation of state curve and plots of various order parameters as a function of volume fraction are shown in Figures S3 and S4 for H*=1.8 and H*=2.0, respectively. At H*=1.8, TC4s show a buckled rhombic that has a
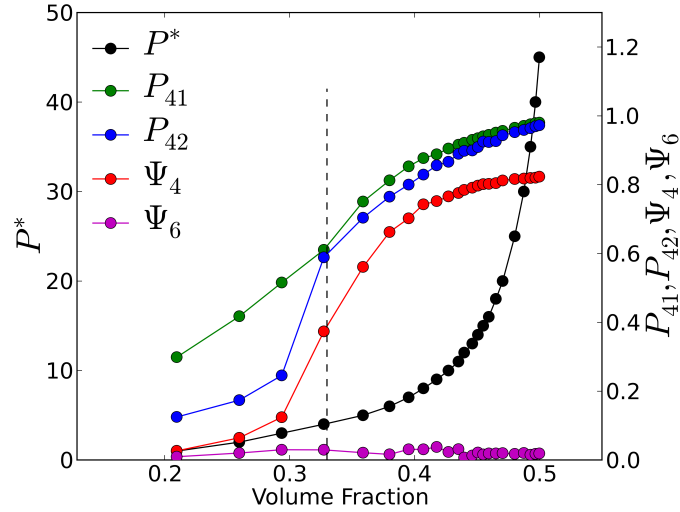
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FIG. S2: Equation of state and concentration dependence of various order parameters for cubes at H* = 1.9. All order parameters are scaled so that they have a maximum value of 1.0. The region between $\phi = 0.33$ to 0.37 has significant particle orientational order and intermediate four-fold bond-orientational order. Dotted line indicates the transition between distinct phases as identified for the phase diagram.

bimodal Z-coordinate particle distribution as shown in the main text. At H* = 2.0, TC4s show a square rotator $(2S_R)$ phase at intermediate volume fractions, as evidenced in Figure S4 where the system gains significant four-fold bond-orientational order at $\phi = 0.39$ while being orientationally disordered. At $\phi \approx 0.47$, TC4s attain moderate orientational order thus leading to a 2S square phase.
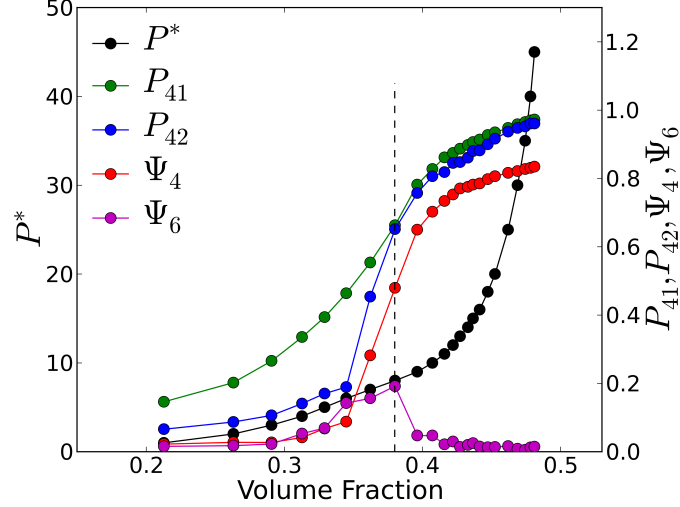

FIG. S3: Equation of state and concentration dependence of various order parameters for TC4s at H* = 1.8. All order parameters are scaled so that they have a maximum value of 1.0. Dotted line indicates the transition between distinct phases as identified for the phase diagram.

III.   CO

Within the confinement range $1.5 < H^* < 1.7$, COs exhibit a hexagonal rotator $(1H_R)$ phase, characterized by high values of Ψ_6 signifying six-fold bond-orientational order but low orientational order (see Figure S5). The $1H_R$ phase
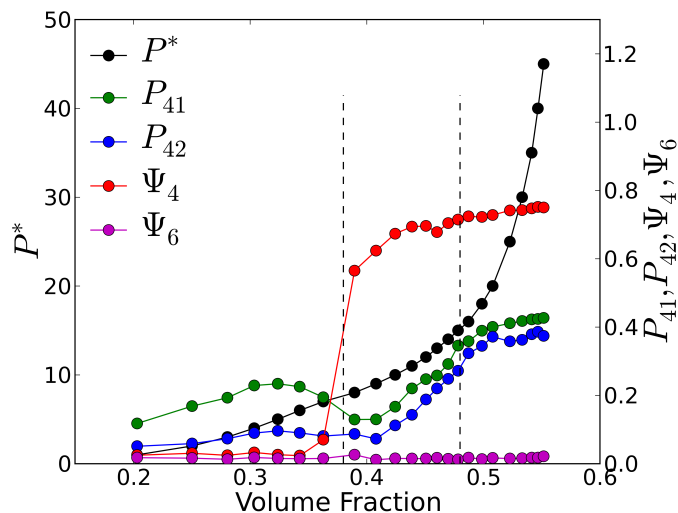
FIG. S4: Equation of state and concentration dependence of various order parameters for TC4s at H* = 2.0. All order parameters are scaled so that they have a maximum value of 1.0. The region $0.39 < \phi < 0.47$ encloses the intermediate $2S_R$ rotator phase. Dotted lines indicate the transition between distinct phases as identified for the phase diagram. Dotted lines indicate the transition between distinct phases as identified for the phase diagram.

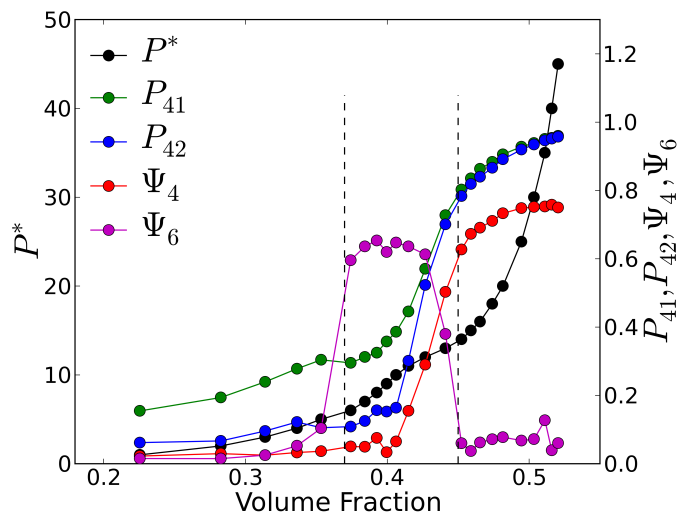eventually gives way to buckled rhombic B_R phase at higher concentrations.

FIG. S5: Equation of state and concentration dependence of various order parameters for COs at H* = 1.5. All order parameters are scaled so that they have a maximum value of 1.0. Dotted lines indicate the transition between distinct phases as identified for the phase diagram.

Such a two-step phase transition is also present for larger values of H*. For $2.6 < H^* < 2.8$ in particular, COs first transition from isotropic to $2H_R$ (a point characterized by a sharp increase in Ψ_6 values) and then continuously transition into a $2R_D$ phase as marked by a steady increase in the orientational order (see Figure S6).

IV. TO

Within the confinement range $1.7 < H^* < 2.0$, TOs form first a square-rotator phase that eventually transitions into a square phase upon compression. This two-step transition can be seen in Figure S7. The system first gains
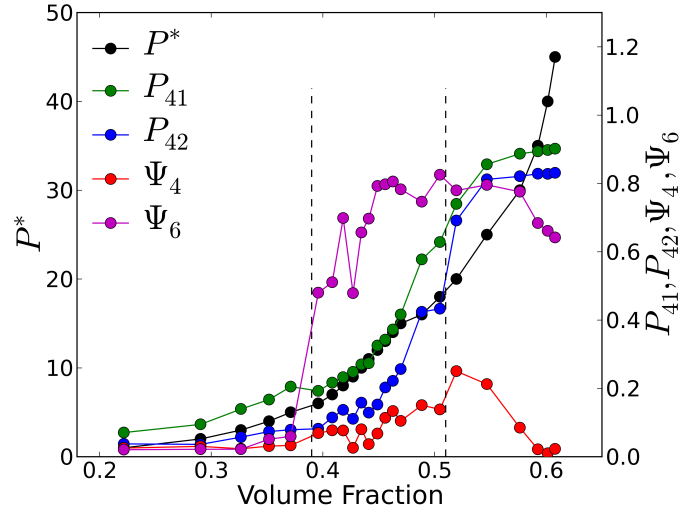
FIG. S6: Equation of state and concentration dependence of various order parameters for COs at H* = 2.8. All order parameters are scaled so that they have a maximum value of 1.0. Two transitions are observed, first from isotropic to $2H_R$ and then from $2H_R$ continuously to $2R_D$. Dotted lines indicate the transition between distinct phases as identified for the phase diagram.

four-fold bond-orientational order at $\phi \approx 0.4$ (as shown by high Ψ_4 values) and then gains orientational order at $\phi \approx 0.56$ (as evidenced by high P_4 values).
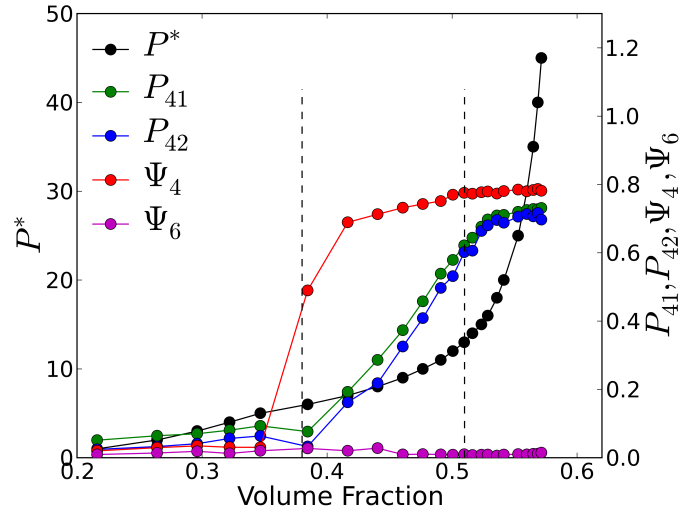

FIG. S7: Equation of state and concentration dependence of various order parameters for TOs at H* = 1.9. All order parameters are scaled so that they have a maximum value of 1.0. Two transitions are observed, first from isotropic to a square rotator $2S_R$ and then from $2S_R$ to 2S square phase. Dotted lines indicate the transition between distinct phases as identified for the phase diagram.

On the other hand, in the $2.1 < H^* < 2.6$ range, TOs only show a single-step transition from isotropic to a two-layer distorted rhombic ($2R_D$) phase. As can be seen in Figure S8, TOs gain both particle orientational order and four-fold bond-orientational order to transition from an isotropic phase into $2R_D$ phase.

Around H*=2.7, a 2-layered buckled square ($2B_S$) phase can be detected. This phase has 4 peaks in its Z-coordinate particle distribution. Figure S9 shows the progression of such distributions at different volume fractions as the system attains the buckled square order. The system, which initially shows bimodal Z-distribution slowly transforms into a quadrimodal distribution. This phase bears a resemblance to BCC structure, both in local coordination as well as its Q_4 and Q_6 order parameters as seen in Figure S10.
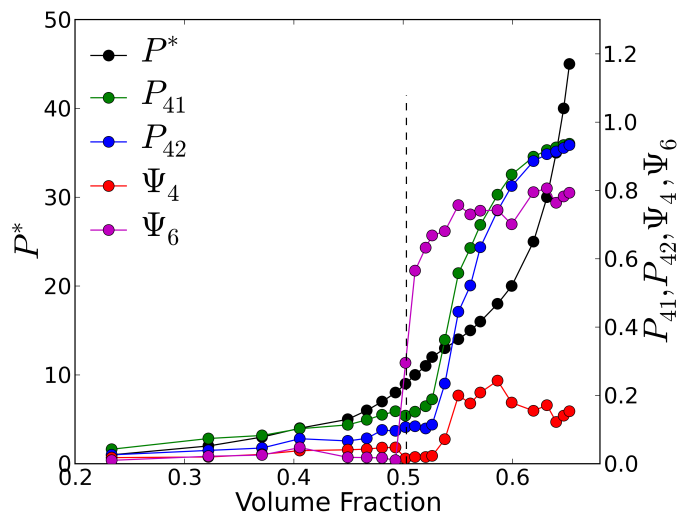
FIG. S8: Equation of state and concentration dependence of various order parameters for TOs at H* = 2.3. All order parameters are scaled so that they have a maximum value of 1.0. A transition is observed from isotropic to a distorted rhombic $2R_D$ phase. Dotted line indicates the transition between distinct phases as identified for the phase diagram.
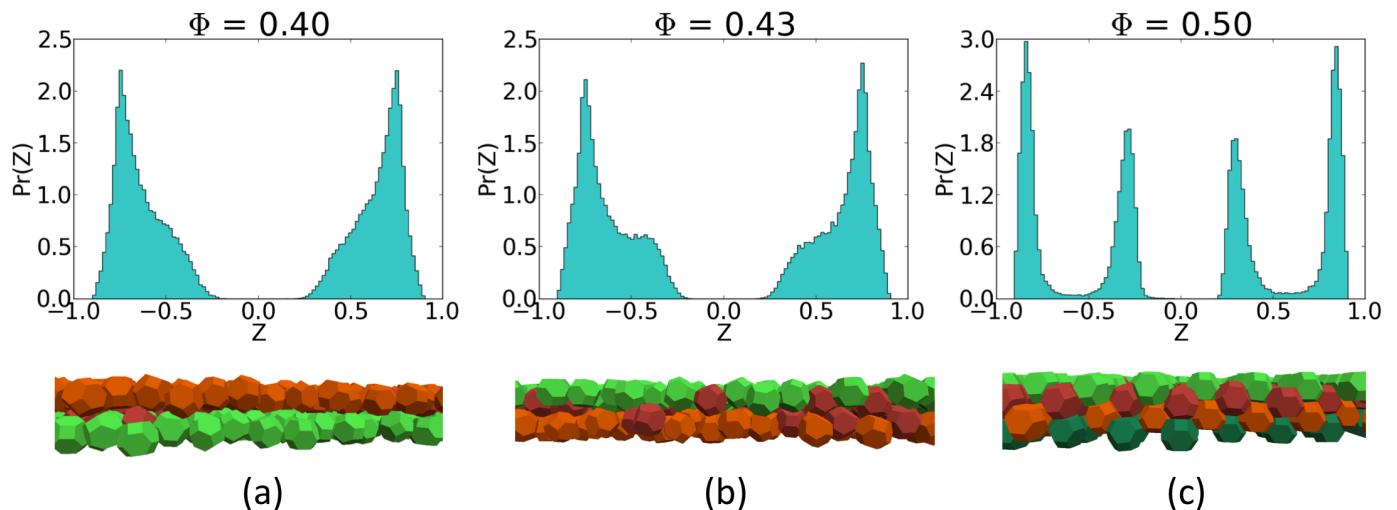

FIG. S9: Z-coordinate particle distributions for a three volume fractions for TOs at H* ≈ 2.7, where they form a buckled square phase. The distribution changes from bimodal to quadrimodal as the system gains $2B_S$ order, which has 2 *nominal* layers. The accompanying side-view snapshots for each case show the layering in the Z-direction.

We note that with increasing number of layers, R_D phases formed by TOs considerably resemble the BCC phase exhibited by TOs in bulk. This can be seen in Figure S11, where for H*= 4.6 we see a combination of low Q_4 and high Q_6 values, which is similar (but not unique) to bulk BCC structure. Additionally, visually, we see that local bond coordination is in 111 direction similar to BCC structure.

[1] B. S. John, C. Juhlin, and F. A. Escobedo, J. Chem Phys. **128**, 044909 (2008).
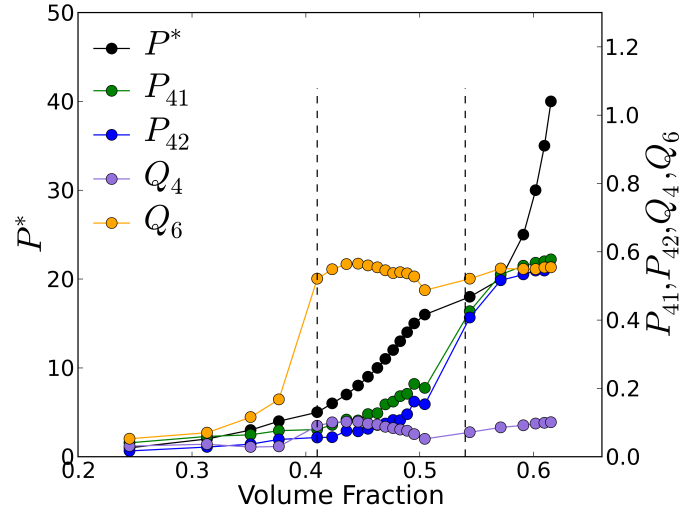[2] U. Agarwal and F. A. Escobedo, Nature materials **10**, 230 (2011).

FIG. S10: Equation of state and concentration dependence of various order parameters for TOs at H* = 2.7. All order parameters are scaled so that they have a maximum value of 1.0 (as against the raw maximum value of 0.588). Dotted lines indicate the transition between distinct phases as identified for the phase diagram.
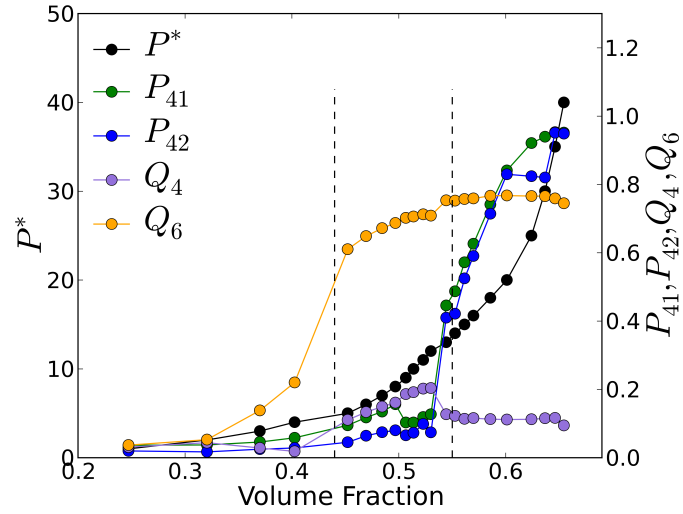

FIG. S11: Equation of state and concentration dependence of various order parameters for TOs at H* = 4.6. All order parameters are scaled so that they have a maximum value of 1.0 (as against the raw maximum value of 0.588). Dotted lines indicate the transition between distinct phases as identified for the phase diagram.