Electronic Supplementary Information for "High antisite defect concentrations in hard-sphere colloidal Laves phases"

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I. FACE-CENTERED-CUBIC CRYSTAL FREE ENERGY INCLUDING SUBSTITUTIONAL DEFECTS

In this section we write down the free energy for the FCC crystal with substitutional defects. Here we do not consider vacancies and interstitials, as it is well-established that the concentration of these point defects is very low [1]. As such they are not expected to change the phase behaviour significantly.

Consider the Helmholtz free energy F_{tot} of a FCC crystal with M lattice sites, N particles, volume V, and temperature T, in which substitutional defects are present. In the following N_{sub} will refer to the number of substitutional defects. As everything here is done at constant T, we will leave out temperature in all following expressions and write:

$$F_{\text{tot}}(M, V, N_{\text{sub}}) = F_0(M, V) + F_d(M, V, N_{\text{sub}}) + F_c(M, N_{\text{sub}}) \tag{S1}$$

with F_0 the defect-free free energy, F_d the free energy of creating N_{sub} non-interacting defects at specific lattice sites, and F_c the combinatorial free energy associated with the number of possible realizations of distributing the defects inside the lattice.

The base free energy is given by

$$F_0(M, V) = M f_0(\rho_M), \tag{S2}$$

where $f_0(\rho_M)$ is the free energy per particle of a defect-free lattice at density $\rho_M = M/V$, which can be calculated for any given density ρ_M using Refs. [2–4].

Next, the total change in free energy associated with the introduction of substitutional defects at specific lattice sites is given by

$$F_d(M, V, N_{\text{sub}}) = N_{\text{sub}} f_{\text{sub}}(\rho_M), \tag{S3}$$

where f_{sub} is the change in free energy associated with creating a single substitutional defect at a specific lattice point. This free energy is again measured in Monte Carlo simulations, by letting one of the particles fluctuate in size, analogous to the method described in the main paper for the Laves phase.

Finally, the combinatorial term in the free energy is given by:

$$\beta F_c(M, N_{\text{sub}}) = -\ln \frac{M!}{(M - N_{\text{sub}})! N_{\text{sub}}!}, \tag{S4}$$

where $\beta = 1/k_B T$ with k_B Boltzmann's constant.

II. EFFECT OF CONFINING PARTICLES TO THEIR WIGNER-SEITZ CELLS

In the simulations in which we measured the defect free energy of a single antisite defect we confined the particles to their Wigner-Seitz cells. Specifically, this prevents the formation of additional defects, and keeps the fluctuating particle at the desired lattice point. Note that we only confined particles to their Wigner-Seitz cells in the simulations in which we measured the defect free energy.

Importantly, confining particles to their Wigner-Seitz cell has no measurable effect on the equation of state, as shown in Figure S1. This can be understood as follows: it is only the center-of-mass of the particle that cannot leave its Wigner-Seitz cell, and, in principle, this still allows the particle to explore a volume much larger than the typical displacements of particles from their lattice point. Hence, restricting the particles to their Wigner-Seitz cells has minimal effect on the accessible phase space, outside of the desired effect of confining the defect to a specific Wigner-Seitz cell.

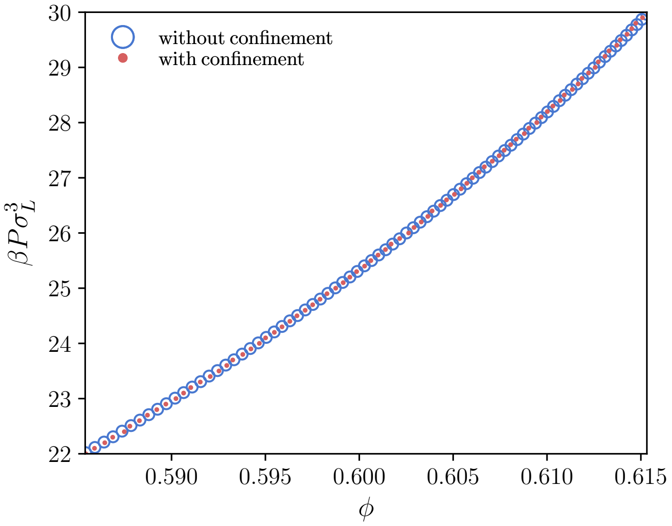

FIG. S1: Comparison of the pressure P as measured in simulations with and without confining particles to their Wigner-Seitz cells. Importantly, restricting the particles to their Wigner-Seitz cells has no measurable effect on the equation of state. Note that the volume fraction on the x-axis is given by $\phi = \frac{N\pi}{6V}\sigma_L^3[(1-x)+xq^3]$, with $q = 0.82$ the size ratio, N the number of particles, V the volume, σ_L the diameter of the large spheres, and $x = \frac{N_s}{N} = \frac{2}{3}$ the composition with N_s the number of small particles.

III. LOW CONCENTRATION OF $\mathrm{L_S}$ ANTISITE DEFECTS

In the main paper, we only considered the possibility of $\mathrm{S_L}$ defects. Here, we justify this approximation. In principle, when both types of defect can be present, even when the volume V, and the number of lattice sites M are held constant, a given composition x can be realized in a number of different ways:

$$x = \frac{2}{3} + \frac{N_{\mathrm{S_L}} - N_{\mathrm{L_S}}}{N}. \tag{S5}$$

Clearly, fixing x only fixes the *difference* between $N_{\mathrm{S_L}}$ and $N_{\mathrm{L_S}}$. Since the combination of x, M, and V determines our state point in the canonical ensemble, the absolute number of defects is a free parameter that is determined by minimizing the Helmholtz free energy.

To estimate the importance of the two types of defects, we plot in Figure S2 the Helmholtz free energy per particle at a fixed composition $x = 0.67$ as a function of the concentration of $\mathrm{L_S}$-defects. Note that for $N_{\mathrm{L_S}} = 0$, the composition requires that 1% of large particles are replaced by a small particle. Clearly from Figure S2, the concentration of $\mathrm{L_S}$-defects that minimizes the free energy is approximately 0.0002, orders of magnitude smaller than the 1% of $\mathrm{S_L}$-defects associated with this composition. Moreover, the difference in the free energy between the equilibrium defect concentration and the concentration with no $\mathrm{L_S}$-defects is less than $0.0005 k_B T$ per particle. Therefore, we can safely ignore $\mathrm{L_S}$-defects because their concentration is so low, and as such they will have a negligible effect on the free energy (and the phase diagram). Note that this was to be expected considering the high cost in free energy associated with introducing $\mathrm{L_S}$-defects (Figure 2 in the main text).

IV. A FIRST-ORDER ESTIMATE OF THE ANTISITE (AND SUBSTITUTIONAL) DEFECT CONCENTRATION

Here, we present a convenient, approximate way to estimate the concentration of antisite or substitutional defects. To this end, we consider a binary crystal at constant pressure P. We now make the approximation that introducing antisite defects has no effect on the equation of state, and again assume that the defects do not interact. In order to allow for the creation of $\mathrm{S_L}$-defects, we put the crystal in contact with a particle reservoir (e.g. a coexisting fluid) with N_S^{res} and N_L^{res} small and large particles, respectively. Note that we only allow the direct exchange of large and small particles between the crystal and the reservoir, so that the total number of particles in each system remains fixed.

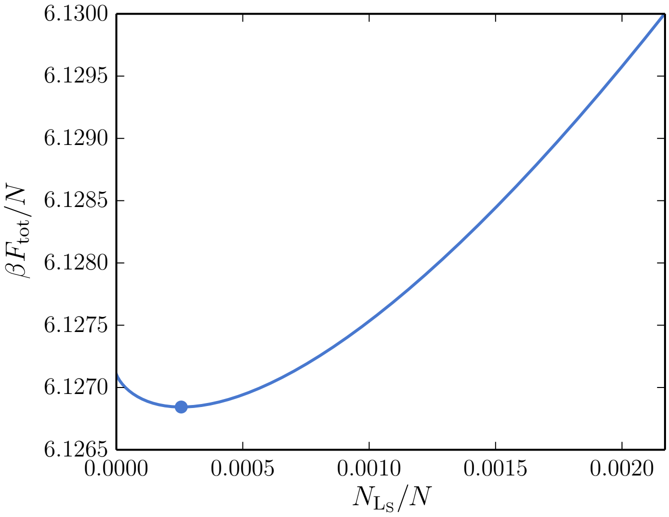

FIG. S2: Helmholtz free energy per particle at a fixed composition $x = 0.67$ as a function of the concentration of L$_\mathrm{S}$-defects. The minimum we observe in the free energy corresponds to a very low concentration of L$_\mathrm{S}$-defects and has a negligible effect on the free energy.

The Gibbs free energy of the full system (crystal plus reservoir), can be written as:

$$G_{\mathrm{sys}}(N_S, N_L, N_{\mathrm{S_L}}, P) \;=\; G_{\mathrm{crys}}(N_S^{\mathrm{crys}}, N_L^{\mathrm{crys}}, P) + G_{\mathrm{res}}(N_S^{\mathrm{res}}, N_L^{\mathrm{res}}, P). \tag{S6}$$

Here, $N_{S(L)}^{\mathrm{crys}}$ and $N_{S(L)}^{\mathrm{res}}$ denote the number of small (large) particles in the crystal and reservoir, respectively, and $N_{S(L)} = N_{S(L)}^{\mathrm{crys}} + N_{S(L)}^{\mathrm{res}}$ is the total number of small (large) particles. Creating an antisite defect corresponds to exchanging a large particle in the crystal for a small particle from the reservoir. We want to minimize the total Gibbs free energy with respect to $N_{\mathrm{S_L}}$. For the reservoir, we can then write:

$$\left(\frac{\partial G_{\mathrm{res}}(N_S^{\mathrm{res}}, N_L^{\mathrm{res}}, P)}{\partial N_{\mathrm{S_L}}}\right)_{N_S, N_L, P} = \mu_L - \mu_S, \tag{S7}$$

where μ_L and μ_S are the chemical potential of the large and small species in the reservoir, respectively.

For the crystal, we Legendre-transform the Gibbs free energy, yielding

$$\begin{aligned} G_{\mathrm{crys}}(N_S^{\mathrm{crys}}, N_L^{\mathrm{crys}}, P) \;&=\; F_{\mathrm{crys}}(N_S^{\mathrm{crys}}, N_L^{\mathrm{crys}}, V) + PV \\ &= M f_0(\rho_M) + N_{\mathrm{S_L}} f_{\mathrm{S_L}}(\rho_M) - k_B T \ln\left(\frac{M_L!}{(M_L - N_{\mathrm{S_L}})! N_{\mathrm{S_L}}!}\right) + PV, \end{aligned} \tag{S8}$$

where $M = N_S^{\mathrm{crys}} + N_L^{\mathrm{crys}}$ and $\rho_M = M/V$ is the density of the defect-free crystal at pressure P. Assuming that the defects do not affect the equation of state of the crystal, $\frac{\partial(PV)}{\partial N_{\mathrm{S_L}}} = 0$. Hence, the derivative of G_{sys} is given by

$$\left(\frac{\partial G_{\mathrm{sys}}(N_S, N_L, N_{\mathrm{S_L}}, P)}{\partial N_{\mathrm{S_L}}}\right)_{N_S, N_L, P} \;=\; g_{\mathrm{S_L}} - k_B T \frac{\partial}{\partial N_{\mathrm{S_L}}} \ln\left(\frac{M_L!}{(M_L - N_{\mathrm{S_L}})! N_{\mathrm{S_L}}!}\right), \tag{S9}$$

where $g_{\mathrm{S_L}} = f_{\mathrm{S_L}} + \mu_L - \mu_S$ is the Gibbs free-energy cost of creating a defect at a specific lattice site. Applying Stirling's approximation and minimizing with respect to $N_{\mathrm{S_L}}$ yields

$$\frac{N_{\mathrm{S_L}}}{M_L} \simeq \exp(-\beta g_{\mathrm{S_L}}), \tag{S10}$$

which provides a straightforward estimate of the effect of defects on the composition of the binary crystal.

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