

Supporting Information for “Fabrication of Colloidal Laves Phases *via* Hard Tetramers and Hard Spheres: Bulk Phase Diagram and Sedimentation Behaviour”

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Free-energy calculations

The bulk phase diagram is determined by using the common tangent construction in the Gibbs free energy g – composition x representation. We remind the reader that the dimensionless Gibbs free energy per particle is defined as $g = \beta G/N = f + Z$, where $f = \beta F/N$ is the dimensionless Helmholtz free energy per particle and $Z = \beta P/\rho = \gamma\beta P/\eta$ is the compressibility factor.

Thus, in order to compute the Gibbs free energy g , one must first calculate the f , and thermodynamic integration is the method of choice for this task.¹ Starting from a reference point, f is obtained by integrating the EOS to the point of interest, assuming no phase

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transition is crossed along the integration path

$$f(\eta) = f(\eta_0) + \frac{\gamma}{k_B T} \int_{\eta_0}^{\eta} d\eta' \frac{P(\eta')}{\eta'^2} \quad (1)$$

The main problem is now shifted to the computation of f at the reference point. For the fluid phase we choose this point to be an ideal gas mixture. For the crystal phases we use the Frenkel-Ladd method extended to account for the anisotropic particle shape.¹⁻⁴ In this method, one connects an Einstein crystal, where particles are tied to their ideal lattice positions and orientations by harmonic springs, to the system of interest by slowly removing the harmonic springs. More details can be found in Ref. 4 and references therein. The Helmholtz free-energy per particle f of a crystal reads:^{3,4}

$$f(\eta_0) = f_{\text{Einst}}(\lambda_{\text{max}}) - \frac{1}{N} \int_0^{\lambda_{\text{max}}} d\lambda' \left\langle \frac{\partial U_{\text{Einst}}(\lambda')}{\partial \lambda'} \right\rangle_{\text{NVT}} \quad (2)$$

where f_{Einst} , which stands for the free energy per particle of an ideal Einstein crystal, is given by:

$$f_{\text{Einst}}(\lambda_{\text{max}}) = -\frac{3(N-1)}{2N} \ln \left(\frac{\pi}{\lambda_{\text{max}}} \right) + \ln \left(\frac{\Lambda_t^3 \Lambda_r}{\sigma_L^3} \right) + \frac{1}{N} \log \left(\frac{\sigma_L^3}{V N^{1/2}} \right) + (1-x) f_{\text{or}}(\lambda_{\text{max}})$$

In Eq. 2, the function $U_{\text{Einst}}(\lambda)$ denotes the harmonic potential that couples the particles positions and orientations to the corresponding Einstein lattice values and reads:

$$\beta U_{\text{Einst}}(\lambda) = \lambda \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{i,0})^2 / \sigma_L^2 + \lambda \sum_{i=1}^{N_t} (\sin^2 \psi_{ia} + \sin^2 \psi_{ib}) \quad (3)$$

where $(\mathbf{r}_i - \mathbf{r}_{i,0})$ represents the displacement of particle i from its position in the ideal Einstein crystal, and where the angles ψ_{ia} and ψ_{ib} are the minimum angles formed by the vector pointing to any of the beads in the tetramer and the rest position of two arbitrarily chosen beads a and b , respectively. Note that all the spheres and tetramers are connected

with springs to their respective lattice positions in the Einstein crystal, whereas an aligning potential is acting only on the tetramers. The term $f_{\text{or}}(\lambda_{\text{max}})$ in Eq. takes into account the orientational free energy of the ideal Einstein crystal and reads:

$$f_{\text{or}}(\lambda_{\text{max}}) = -\ln \left\{ \frac{1}{8\pi^2} \int d\phi d\theta d\chi \sin(\theta) \exp \left[-\lambda_{\text{max}} (\sin^2 \psi_{ia} + \sin^2 \psi_{ib}) \right] \right\} \quad (4)$$

where ϕ , θ and χ are the Euler angles. This integral depends only on the maximum value chosen for the coupling constant λ and, of course, on the form of the Hamiltonian chosen for the orientational springs. In simple cases, it can be evaluated exactly or in an approximated analytic form. However, when the orientational Hamiltonian is more complex as in the current case, it must be calculated numerically, *e.g.* through MC integration.

Once the Helmholtz free energy is known, the Gibbs free energy per particle for fixed composition and varying pressure is calculated as

$$g(P, x) = f(\eta_0, x) + \gamma \int_{\eta_0}^{\eta} d\eta' \frac{\beta P(\eta', x)}{\eta'^2} + Z(P, x) \quad (5)$$

With the outlined procedure, we calculate the Gibbs free energy $g(P, x)$ for the fluid phase at different compositions with a grid spacing of 0.1, as well as the Gibbs free energy $g(P, x)$ for the solid phases. We then use the common tangent construction in the (g, x) -plane to draw the phase diagram. A representative calculation of $g(P, x)$ is given in Fig. 1, where we also show the results of the common tangent construction. By collecting the information about $g(P, x)$ at several pressure values, we eventually map out the phase diagram of the binary mixture in the pressure $\beta P \sigma_L^3$ – sphere composition x representation.

References

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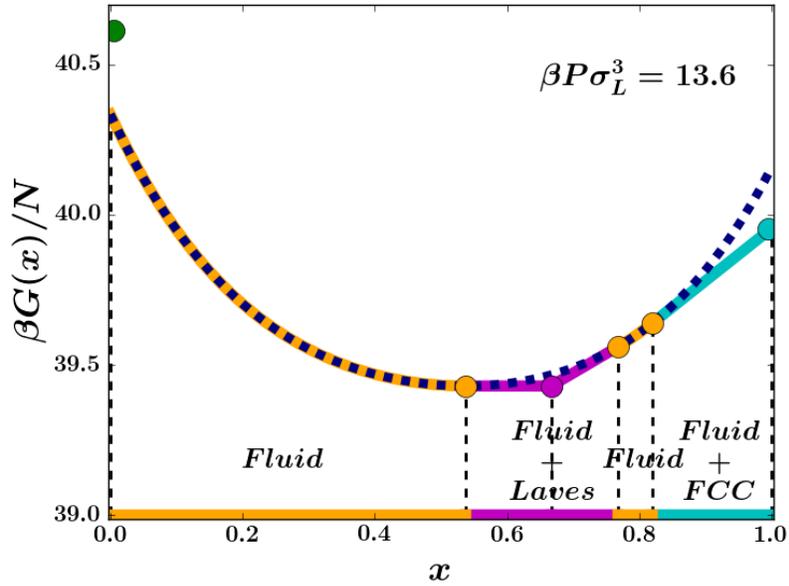


Figure 1: Gibbs free energy per particle $g = \beta G(P, x)/N$ as function of composition $x = N_s/N$ for a fixed pressure $\beta P \sigma_L^3 = 13.6$. The green, magenta and cyan dots represent the SC phase of pure tetramers (at $x = 0$), the LP1 crystal (at $x = 2/3$), and the FCC of pure large spheres (at $x = 1$), respectively. The blue dashed line shows the Gibbs free energy $g(P, x)$ of the fluid as function of composition x . The orange dots represent the coexistence points between the fluid and the LP1 crystal (2 points), and between the fluid and the FCC crystal of pure large spheres, as calculated by the common tangent construction. The thick lines show the path of minimal Gibbs free-energy.

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