

Growth and Interaction of Colloid Nuclei under Microgravity



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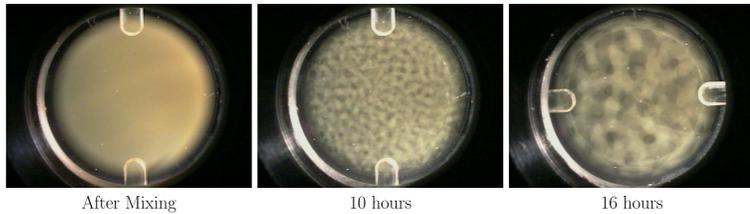


Abstract

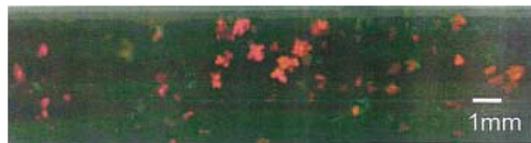
We have developed a model describing the growth of colloid nuclei. The model is based on a coupled diffusion problem for the solid and liquid phase, combined with the consistent boundary conditions involving osmotic pressure balance, including interfacial tension. The motion of the solidification front is modeled based on the Wilson-Frenkel law. Our improved model allows for direct comparison with the experiments. To illustrate this point, comparison with and interpretation of the data obtained on the ISS, as well as in ground-based experiments, is discussed.

Experiments

Various experiments on phase transition in hard-sphere colloids have been performed; however, under gravity, sedimentation due to gravity dominates crystal growth, obscuring crystal growth due to phase transition. Therefore, more recent experiments have been performed aboard the ISS (microgravity), to remove the effects of sedimentation.



Colloid-polymer mixture undergoing spinodal decomposition in microgravity. Source: NASA Physical Science Informatics (PSI) data repository.



Crystal growth of hard spheres under microgravity. Source: Cheng et al. [2].

Governing Equations

Nondimensionalization:

To nondimensionalize, we choose to scale:

- spatial dimensions by the particle radius \hat{a}
- diffusivities (to be discussed) by Stokes-Einstein diffusion, \hat{D}_0
- time by the time scale associated with Stokes-Einstein diffusivity, $\tau = \hat{D}_0/\hat{a}^2$

Diffusion Coefficients:

- D_s : Short time diffusivity
 - D_l : Long time diffusivity
 - $D_{c,f}$: Collective diffusivity in liquid phase
 - $D_{c,s}$: Collective diffusivity in solid phase
- Following [9], the collective diffusivities are related to fluxes in the chemical potentials (discussed in next column), specifically,

$$D_{c,f} = D_l(\varphi)\mu'_f(\varphi) \quad \text{and} \quad D_{c,s} = D_s(\varphi)\mu'_s(\varphi), \quad (1)$$

and the short and long time diffusion are fitted to experimental data by van Megen et al. [5].

Bulk Equations: To model the growth of a solid crystal suspended (dispersed phase) in a liquid (dispersion medium), we assume that diffusion dominates the dynamics in both crystal and liquid state. Assuming furthermore that there are no relevant external forces (e.g., gravity), the evolution of the volume fractions in the crystal, φ_s , and liquid, φ_f , states are governed by the (nonlinear) diffusion equations as follows

$$\frac{\partial \varphi_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_{c,s}(\varphi_f) \frac{\partial \varphi_s}{\partial r} \right] \quad r \in [0, X(t)] \quad \text{and} \quad \frac{\partial \varphi_f}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_{c,f}(\varphi_f) \frac{\partial \varphi_f}{\partial r} \right] \quad r \in [X(t), L]. \quad (2)$$

where $X(t)$ is interface between the crystal state (inner core) and surrounding fluid state, and L is the size of the entire domain.

Boundary Conditions at the Front:

- Osmotic Pressure Balance

$$\Pi_s(\varphi_s) = \Pi_f(\varphi_f) + \frac{\Gamma}{X}, \quad \Gamma = \frac{8\pi}{3} \frac{a^2}{k_b T} \gamma_{fs} = \frac{8\pi}{3} \hat{\Gamma} \quad (3)$$

where Π_s and Π_f are scaled osmotic pressures in the crystal and liquid state, respectively; Γ is a measure of the (nondimensional) surface tension force. Following [6], $\hat{\Gamma} = 0.15$.

- Wilson-Frenkel Law (Kinematics)

$$\frac{dX}{dt} = \alpha \frac{D_s(\varphi_f)}{2} J, \quad J = 1 - e^F, \quad F = \mu_s(\varphi_s) - \mu_f(\varphi_f) + \frac{\Gamma}{\varphi_s X}, \quad (4)$$

where μ_s and μ_f are scaled chemical potentials in the crystal and liquid state, respectively; and we will also consider using D_l instead of D_s in (4).

- Conservation of Mass/Kinematics Balance

$$D_{c,f}(\varphi_{fX}) \frac{\partial \varphi_{fX}}{\partial r} - D_{c,s}(\varphi_{sX}) \frac{\partial \varphi_{sX}}{\partial r} = (\varphi_{sX} - \varphi_{fX}) \alpha \frac{D_s(\varphi_{fX})}{2} J, \quad (5)$$

References

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Equation of State: The osmotic pressures and chemical potentials may be expressed in terms of a compressibility factor, Z .

$$\mu(\varphi) = \int \frac{Z(\varphi)}{\varphi} d\varphi + Z(\varphi) + c \quad \text{and} \quad \Pi(\varphi) = \varphi Z(\varphi), \quad (6)$$

where we choose Z to match experimental results of Speedy [7,8].

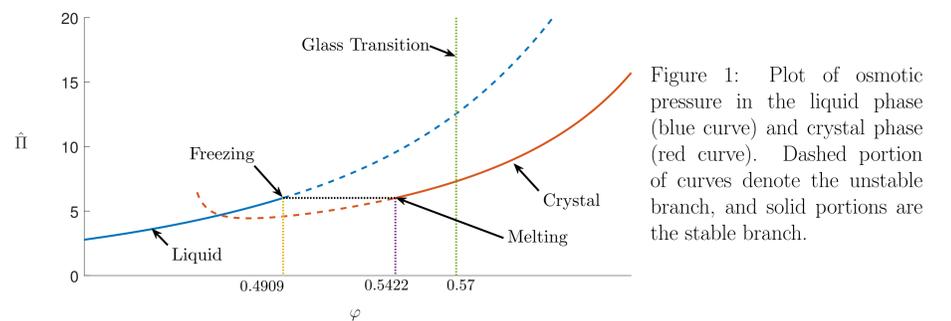


Figure 1: Plot of osmotic pressure in the liquid phase (blue curve) and crystal phase (red curve). Dashed portion of curves denote the unstable branch, and solid portions are the stable branch.

New Features: Our model includes several new features not considered in previous model, e.g. Ackerson et al. [1] and Russel et al. [6].

- Relating diffusivity in bulk to chemical potentials, see (1).
- Accurate numerical treatment of the boundary conditions at the front, see (3)-(5).
- Including functional dependence of diffusion on the volume fraction in Wilson-Frenkel law, see (4).

These new features reduce the free parameters in our model to one, α .

Comparison to Experiments

Goal: We investigate the values of α that are compatible with the experimental results. Specifically, we neglect the effects of the diffusion layer and assume that crystal interactions occur when the crystal size in simulations reaches the maximum crystal size from experiments (based on the number of crystals experimentally measured). We then search for a value of α such that the maximum crystal size is achieved at the start of the ripening phase measured in experiments.

We consider three experimental results in our comparisons: 1) microgravity experiments by Cheng et al. [2], and density-matched experiments by Harland et al. [3] and Iacopini et al. [4]. Furthermore, we only consider volume fraction above the melting point (one-phase regime) and below the glass transition, i.e., between vertical dotted purple line and green line in Fig. 1.

Procedure: For each experiment,

- We run simulations for various values of α
- Extract the time when the maximum crystal size is reached, t_i , see Fig 2.
- Construct t_i as a function of α , and use interpolation to estimate α at the start of the ripening phase measure in experiments, see Fig. 3a.

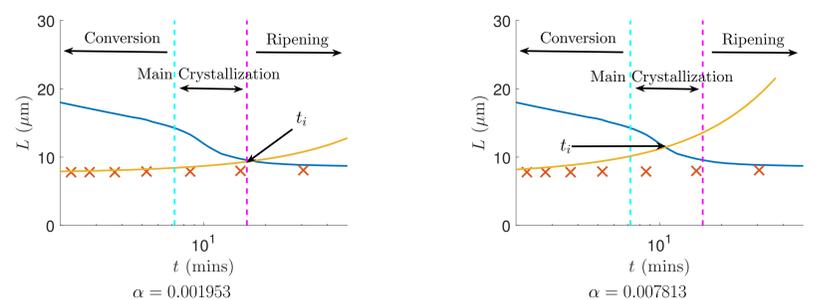


Figure 2: Comparison between experiments in Harland et al. [3] for $\varphi = 0.565$.

- Blue Curve - Maximum Average Crystal size based on experimental measurements of number of crystals.
- Red Crosses - Average crystal size measured in experiments.
- Yellow Curve - Crystal size from simulations.

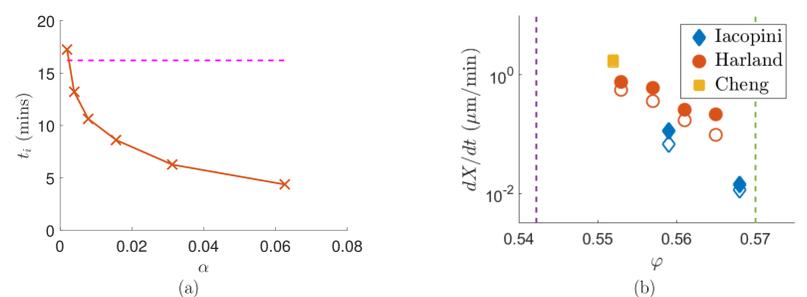


Figure 3: a) The time corresponding to maximum crystal size, t_i , as a function of α , extracted from the comparison of simulations and experiments in Fig 2. b) The rate of crystal growth as a function of the volume fraction at the start of the ripening phase with short diffusivity (solid symbols) and long diffusivity (hollow symbols) in the Wilson-Frenkel law (4).

Conclusion

Our improved modeling and accurate simulations allow for direct comparison with experiments carried out at the ISS and under gravity. The model includes a single unknown parameter determining the rate of crystal growth, that has been determined by comparison with the experiments. Future work will be to include interaction between nuclei, and to carry out analysis for the two phase regime.

Acknowledgements

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