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A Smoluchowski Model of Colloidal Crystallization Dynamics

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1. Introduction

Understanding concentrated colloidal dynamics in the presence of different pairwise interactions and external fields provides a basis to predict the temporal evolution of colloidal microstructures in diverse phenomena including suspension rheology and colloidal crystallization. However, a microscopic theory of concentrated colloidal dynamics does not yet exist that rigorously includes both statistical mechanical (configuration dependent free energy changes) and fluid mechanical (configuration dependent multi-body hydrodynamic interactions) contributions.

The goal of the present work is to generate a coarse-grained dynamic, as well as equilibrium, model for the phase behavior of a model colloidal crystallizing system. The basis of our model is the Smoluchowski equation (SE), a partial differential equation whose solution is the probability density of a stochastic system in a set of observable (order parameter) variables. Several order parameters are studied to describe the dynamic crystallization process. One-dimensional and two-dimensional descriptions of the model system are studied. The values of the free energies (i.e. the free energy landscape, FEL) and diffusivities (i.e. the diffusivity landscapes) of the SE, which provide a complete dynamic description of the system, were determined by analyzing, according to previously described statistical procedures, [1,2] ensembles of short-time trajectories from Brownian Dynamics (BD) and Stokesian Dynamics (SD) simulations on the system under the conditions of interest. The SE models are then compared with Monte Carlo-Umbrella Sampling (MC-US) and BD and SD simulations (FEL from equilibrium analyses and mean first passage times, MFPT, from dynamic analyses).

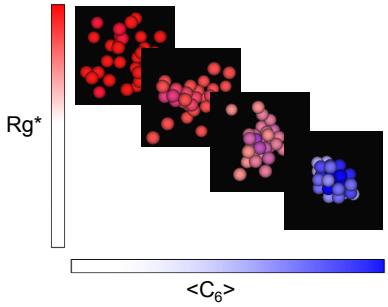

Fig 1. Model colloidal system renderings as function of condensation (Rg^*) and crystallinity ($\langle C_6 \rangle$) order parameters. Particle coloring scheme combines a white-red scale for Rg^* and a white-blue scale for $\langle C_6 \rangle$.

2. Preliminary Results

Two order parameters were found to describe important features in colloidal crystallization. Fig 1 shows renderings of a model colloidal crystallizing system referenced to different levels of the order parameters. System expansion (Rg^*) and

crystallinity (<C_6>) were found by means of a search through several order parameters, domain expertise and pre-eminence in the literature[frenkel, karplus].

With known order parameters, FEL at different interaction strengths were found by means of MC-US simulations, and are shown schematically in Fig 2. 6 different interaction strengths are shown (normalized respect to coexistence conditions Π_m) [3] and the resulting FEL show important features in colloidal crystallization, such as the existence of multiple minima at high interaction strengths, and transition states at low saturations.

Dynamic analyses are performed by means of linear fitting of short time approximations of Smoluchowski equation coefficients (Linear Fit, LF)[1] and Bayesian inference from dynamic simulation observations (BI)[2]. Our results show the limit of applicability of LF, and the need to use a 2D description to correctly capture dynamics [4].

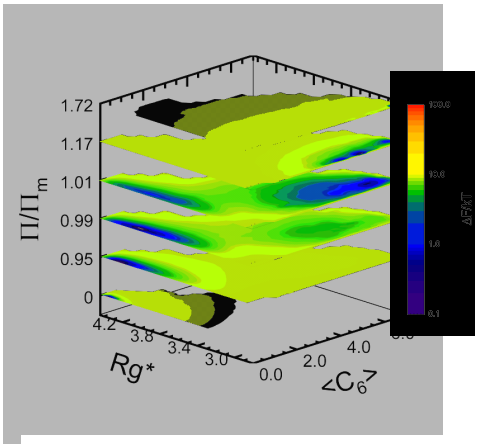

Fig 2. FEL obtained from MC-US simulations for varying interparticle attraction (Π), normalized respect to coexistence conditions (Π_m) in terms of condensation (Rg^*) and crystallinity (<C_6>) order parameters. Free energy scale is show in the side bar. The Free energy reference was taken as 0 for the minimum at each condition.

3. Conclusion

After identifying appropriate order parameters to monitor colloidal crystallization, we first show that umbrella sampling methods in conjunction with Monte Carlo simulations produce the same free energy landscapes as our SE analysis of Brownian Dynamic (BD) and Stokesian Dynamic (SD) simulations. Our results show the limits of applicability of the different analysis schemes to extract FEL and DL. We demonstrate the use of these landscapes in the SE model for describing first passage times between different states as a means to control colloidal crystal assembly processes via open- and closed- loop control schemes that produce defect free single colloidal crystals.

References

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