Abstract

Microscopic nature of nuclei and extremely fast nucleation events makes it difficult to study nucleation experimentally. Route to nucleation can be effected by different parameters such as thermodynamic conditions, fluid phase composition and surface heterogeneity etc. The focus of this thesis is on investigating competing pathways of crystal nucleation in variety of systems. In this thesis, we use molecular simulations to study crystal nucleation in model systems. These model systems mimic real systems such as colloidal systems and globular proteins very closely. Advances in computational power and rare event sampling methods help us in better understanding of underlying mechanism involved in nucleation phenomena.

Proteins are hard to crystallize and high quality of protein crystals desired for their structural determination. One way to promote protein crystallization is heterogeneously using substrates. In our study, we focus on the effect of nano-wrinkled surfaces on nucleation of model globular proteins such as lysozyme. We computed free-energy barriers for homogeneous nucleation and heterogeneous nucleation of proteins on flat and wrinkled surfaces. The study reveals that, the enhancement of nucleation in presence of wrinkled surface is closely related to the two step nucleation process seen during protein crystallization. There is an enhancement of protein concentration near trough of the wrinkled surface which aid in nucleation. However, the high curvature at the trough acts as a deterrent to crystal nucleus formation. Hence, significant lowering of the free-

energy barrier is seen only if the increase in the protein concentration at the trough is very high.

Co-crystals also known as substituionally ordered solid compounds forms when two or more different compounds combine in a stoichiometric ratio. We investigate the effect of fluid phase composition on homogeneous nucleation of AB_2 co-crystal. In this work we made a comparative study between nucleation of metastable AB_2 solid and pure A solid with FCC structure. Our simulation results show that the nucleation of AB_2 solid is favoured even under conditions where the pure A solid is more stable. This is primarily due to similarity in the composition of fluid-phase and the AB_2 type solid which in turn leads to much lower interfacial tension between the crystal nucleus and the fluid phase.

Interfacial free energy is a fundamental thermodynamic quantity determines the rate of formation of nuclei from fluid phase. It also determines the barrier for formation of nuclei. In binary mixtures, intefacial free energy has a strong dependence on fluid composition. We presented a simple method to compute the effect of fluid phase composition on interfacial free energy of binary hard sphere mixtures. In this method interfacial free energy is calculated by numerically integrating Gibbs adsorption isotherm. Surface excess quantities are computed from simulation and phase equilibrium data. Our calculations indicates intrefacial free energies for binary mixtures are higher than that of pure component interfacial free energies. Our calculations of interfacial free energy are consistent for different system sizes studied.