4by Monte Carlo Simulation Study of Binary Hard Sphere Crystallization

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Although crystal nucleation is an important phenomenon in many processes, our understanding of its molecular mechanism remains incomplete. There has been a number of studies on crystallization that have led to an ever increasing understanding of the mechanism of nucleation. Nevertheless many open questions concerning crystallization phenomena still remain including the rate of formation of the crystal phase, structure and composition of the critical nucleus, role of solvents and foreign objects etc. Crystals can exhibit many structures of which only one structure is the most stable one. However it is not known a priori which structure will form upon nucleation. Ostwald's[1] rule of stages states that the crystal phase that nucleates from a supercooled liquid is the one that is closest to liquid state in its free energy. Hence crystallization via nucleation may yield the metastable form instead of the most stable structure. This is issue is particularly important, for example, in the pharmaceutical industry where the same drug molecule can have different properties due to differences in its crystal structure. Hard sphere systems represent the simplest models which show order-disorder transition. They are also the most extensively studied systems. Their thermodynamic properties and phase diagrams are well known. Based on a survey of the data for phase diagrams for binary organic mixtures, Matsuoka was able to classify them into six different types[2]. Binary hard sphere systems are capable of exhibiting five of those six types of phase diagrams. Binary hard sphere crystals are capable of showing a rich variety of morphologies including the formation of substitutionally ordered crystal structures such as AB, AB2 and AB13[3-5]. The molecular mechanism for the formation of these phases are unknown. Experiments of binary mixtures of colloidal particles have shown the formation of metastable crystal structures[6] which provide evidence for the manifestation of the Ostwald's rule. In order to understand the molecular mechanism of crystallization we study on crystal nucleation in a binary hard sphere system via Monte Carlo simulations. We use the umbrella sampling technique to study the formation of the critical nucleus during crystallization. The simulation allows us to perform a detailed analysis of the structure and the composition of the critical nucleus. The results show that the crystal nuclei not only differs from the liquid phase in composition but also in their structure.

1.W. Ostwald, Z. Phys. Chem. 22, 289 (1897).

2.M. Matsuoka, Bunri Gijutsu (Separation Process Engineering), 7, 245 (1997).

3.X. Cottin and P. A. Monson, J. Chem. Phys. 102, 3354, (1995).

4.M. D. Eldridge, P. A. Madden, P. N. Pusey, and P. Bartlett, Mol. Phys. 84, 295 (1995).

5.P. Bartlett, J. Phys.: Condens. Matter 2, 4979 (1990).

6.A. Schofield Phys. Rev. E 64, 051403 (2001).