

Study on heterogeneous nucleation of colloidal crystals: the effect of interfacial free energy on nucleation process

著者	GUO Suxia
number	84
学位授与機関	Tohoku University
学位授与番号	理博第3203号
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論文内容要旨

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氏名	郭素霞	提出年	平成30年
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論 文 內 容 要 旨

This thesis focuses on heterogeneous nucleation of two-dimensional (2D) colloidal crystals on the substrate. Though there is long research history on the nucleation, mechanism of the nucleation remains still unclear due to the limitations of eligible experimental evidence; the process occurs in quite short time and small length scale. To gain a better understanding of the nucleation process, colloidal crystals are employed as a model to study the nucleation. The outline of this thesis is as follows.

In chapter 1, studies of the nucleation were reviewed, and the classical nucleation theory (CNT) was described. The studies of colloidal crystals applied to the nucleation study were also reviewed, pointing out that the substrate effect has not been taken into account in those studies.

In chapter 2, the principle of colloidal crystallization was introduced. In particular, detailed mechanism of the depletion attraction was described, which was employed in the present study.

In chapter 3, the heterogeneous nucleation of colloidal crystals on a cover glass was described. Based on the *in situ* observations, we have found two types of nucleation processes: a cluster that overcomes the critical size for nucleation with a mono-layer, and a method that occurs with two layers, which was defined as quasi-2D nucleation. This quasi-2D nucleation process has been firstly reported in the present study. The Gibbs free energy changes (ΔG) for these two types of nucleation processes were evaluated by taking into account the interfacial free energy, $\Delta\sigma$, as an effect of substrate. The ΔG calculation suggests that ΔG of q-2D nucleation is smaller than that for mono-layer nucleation at a given particle concentration. Introduction of $\Delta\sigma$ into the ΔG calculation accounts for occurrence of the quasi-2D nucleation in the experiment.

In chapter 4, the effect of the substrate as $\Delta\sigma$ on the nucleation rate of colloidal crystals was discussed. The nucleation processes on uncoated, Au-coated, and Pt-coated cover glass under the same particle concentration were examined. The nucleation rate, J , on the three substrates as a function of particle concentration was measured. The values of $\Delta\sigma$ for three substrates were obtained based on equation of the CNT, indicating that cover glass possess smallest $\Delta\sigma$ while it was largest for the Pt-coated cover glass. Since the $\Delta\sigma$ originates from bonding energy between substrate and crystals in the atomic system, we deduce that the magnitude of $\Delta\sigma$ is related to the strength of interaction between particles and substrate. The surface force measurements for each substrate were conducted by atomic force microscopy (AFM) equipped with colloidal probe. The order of strength of the interaction was found to be consistent with the order of the magnitude of $\Delta\sigma$ on three substrates. The value of $\Delta\sigma$ was determined by interaction between colloidal particles and substrate, which in turn changes the nucleation rate.

In chapter 5, the conclusion of the thesis was presented. We have successfully revealed the detailed nucleation process of 2D colloidal crystals on the substrates. Our observations indicate the occurrence of quasi-2D nucleation, which is a new nucleation process. The substrate effect, $\Delta\sigma$, was quantitatively evaluated and identified to play a crucial role in nucleation of colloidal crystals. The magnitude of $\Delta\sigma$ is related to the strength of the interaction between particles and each substrate, which was confirmed via surface force measurements. These findings will contribute to the basic understanding of the heterogeneous nucleation on the substrates.

論文審査の結果の要旨

コロイド粒子は溶液中で熱運動し原子や分子と同様に相転移を示すため、相転移に関わる様々な物理現象のモデルとして有効である。核形成は材料科学において最も基礎的な相転移現象でありながら、非常に短時間かつ微小サイズの現象であるためその理解は未だ充分ではない。本研究は包括的な核形成の理解を得る事を目的とし、2次元コロイド結晶を用いて核形成プロセスを明らかにする実験と解析を行った。

第1章では核形成の研究について概説し、核形成の解析に広く用いられている古典的核形成理論について述べている。また、コロイド結晶を用いた核形成研究について述べ、核形成に与える基板の効果が考慮されてこなかった点を明らかにした。

第2章では本研究で用いた結晶育成法について述べている。コロイド結晶化の原理、特に本研究で用いた枯渴引力法について詳述している。

第3章ではコロイド結晶のガラス基板への2次元核形成について述べている。その場観察の結果、2種類の核形成プロセスを明らかにした。2次元核形成が1層で起きる従来型のもの、臨界核以下のサイズで2層となりそのまま核形成するもの(quasi-two-dimensional (q-2D) nucleation)である。q-2D nucleation は本研究で初めて明らかになった2次元核形成モードである。すなわち、q-2D nucleationの方が1層による核形成より少ない粒子数で核形成する事を見出した。q-2D nucleationに伴う自由エネルギー変化のモデルを構築し、実験的に見積もった種々のパラメータからその値を計算した。基板の効果である界面自由エネルギー($\Delta\sigma$)を導入することで初めて q-2D nucleation がエネルギー的に有利である事を示し、実験結果を整合的に説明した。

第4章では異なる基板に対する核形成頻度の変化を明らかにした。カバーガラス、Au または Pt をコーティングしたカバーガラスの3種類の基板を用いた。核形成頻度は Pt、Au、カバーガラスの順に大きくなった。核形成頻度から見積もられた $\Delta\sigma$ はカバーガラス、Au、Ptの順に値が大きくなる。原子間力顕微鏡にコロイドプローブを用いた表面間力測定により溶液中の粒子と各基板間との相互作用を測定し、相互作用が大きいほど大きな $\Delta\sigma$ を持つ事を明らかにした。すなわち、基板と粒子間の相互作用により $\Delta\sigma$ が決まり、その値によって核形成頻度が増える事を示した。

以上の研究成果は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、郭素霞提出の博士論文は博士(理学)の学位論文として合格と認める。