

HW2. A comparison between classical and non-classical nucleation theories

The comparison through paper review

“A Review of Classical and Nonclassical Nucleation Theories”

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What contents here..

1. Introduction

The classical path way to nucleation which was once considered to have general applicability to all nucleating system is gradually giving way to a nonclassical pathway which is now considered as a dominating mechanism in solution crystallization and other systems. In this review, an attempt is made to compare underlying physical principles involved in various nucleating systems and their theoretical treatment based on classical nucleation theory, and other important theories such as a density functional approach and diffuse interface theory. The limitation of classical theory, the gradual evolution of nonclassical two-step pathway to nucleation, and the questions that must be addressed in the future are discussed systematically.

2. Nucleation theories

2.1 Classical nucleation theory (CNT)

CNT is most common theoretical model used to understand nucleation of a new thermodynamic phase such as liquid and solid. The CNT is based on condensation of vapor of liquid which can be extended to other liquid-solid equilibrium systems such as crystallization from melts and solutions as well. The change in the free energy of the system during homogeneous nucleation of a spherical nucleus of radius r is given by

$$\Delta G = \frac{-4\pi r^3}{3\nu}KT \ln S + 4\pi r^2\sigma$$

First term : # of molecules in a cluster radius r

$S = P/P^*$ (vapor saturation ratio)

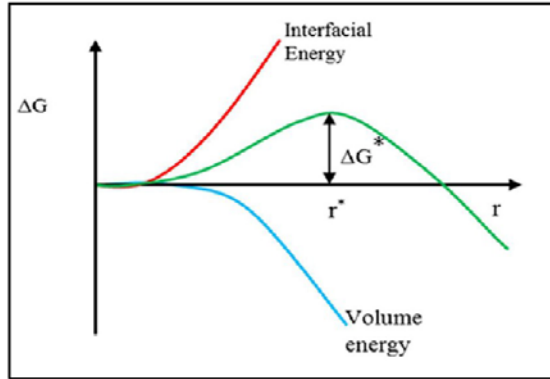


Figure 1. Schematic representation showing the dependence of nucleation barrier ΔG^* on the radius r according to classical nucleation theory.

Simplifying assumptions of CNT are

- (a) The nucleus can be described with the same macroscopic properties (density, structure, composition) of the stable phase
- (b) The nucleus is spherical and the interface between the nucleus and the solution is a sharp boundary
- (c) Vapor-liquid interface is approximated as planar, regardless of critical cluster size

If polymorphism is expected for a system, it may not necessarily nucleate in the stable form, but passes through a path in which the free energy barrier is minimum, which is not taken into account by CNT. Even though the theory is able to capture the underlying physics of the phenomena and provide good qualitative interpretation of nucleation data, its failure to provide a correct quantitative description led to the failure CNT for a variety of systems. Another shortcoming of the theory is that it is unable to explain the vanishing nucleation barrier at high supersaturations. In spite of various extensions and developments in theoretical approaches, CNT still serves as a platform to describe nucleation, since it is based on experimentally accessible information.

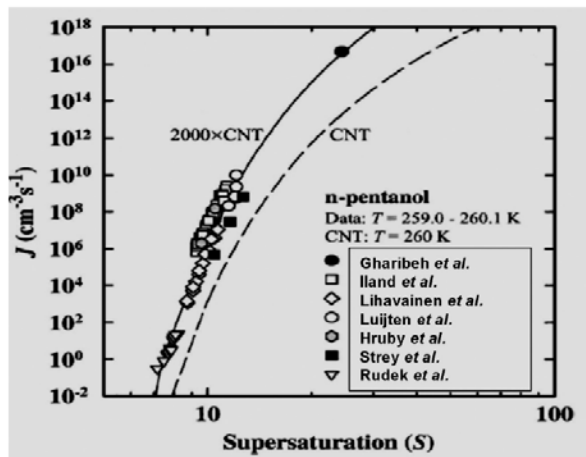


Figure 3. Comparison of nucleation rates of *n*-pentanol reported by various research groups. Dashed lines represent predictions by CNT, and the solid line corresponds to the predictions of CNT, multiplied by 2000 [ref 44–49 and 43 as per the order of authors mentioned in figure]. (Reproduced with permission from ref 44. Copyright 2005 AIP Publishing LLC.)

2.2 ~ 2.5 : Predictions of CNT in various systems such as vapor-liquid system, metallic vapor system, glass system and supercooled liquid metals and alloy systems.

3. Fusion of extended modified liquid drop model with dynamic nucleation theory (EMLD-DNT)

One of the successful modifications of CNT is the extended modified liquid drop (EMLD) model proposed by Reguera et al.⁸⁰ which does not need any information on intermolecular potential like other molecular theories and accurately describes the properties of very small confined systems. The contribution to the free energy of formation by the translating drop in the container and the effect of fluctuation in “ n ” of a system of few molecules are incorporated in the EMLD model.

4. Density Functional Theory (DFT)

Another popular approach to study the vapor-liquid equilibria is based on microscopic molecular interaction which avoids the capillary approximations of CNT. The DFT also sometimes referred to as nonclassical theory is a powerful tool to analyze various vapor-liquid, liquid-solid nucleation phenomena, and it also able to predict the spinodal. DFT which was originally developed by Oxtoby, Evans, and Zeng approached the problem based on a density functional approach which expresses the intrinsic free energy of the system as the function of molecular number density. The theory assumes that the free energy of nucleus $\Delta\Omega_{\text{DFT}}$ (same as ΔG^*) depends on the average spherical density profile rather than the radius.

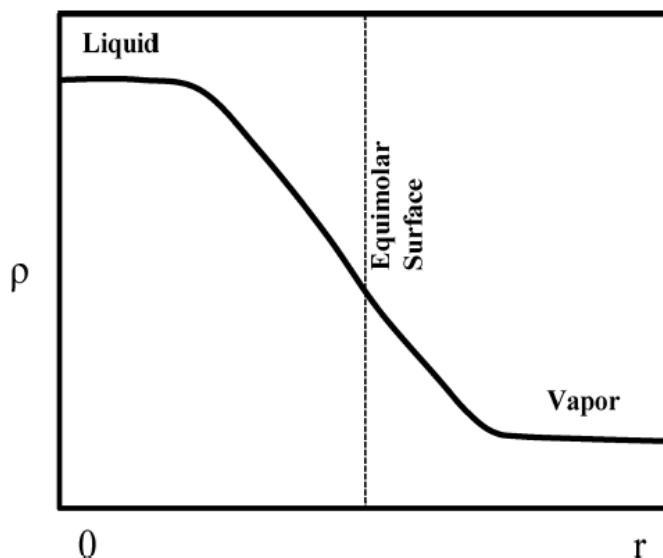


Figure 8. Density profile $\rho(r)$ of the nucleus of the vapor-liquid system changing from liquid-like at the center to the bulk vapor density far from it.

5. Diffuse Interface Theory (DIT)

The predictions of CNT show an error of several orders of magnitude for the experimental vapor condensation data due to the assumption that the thickness of interface is small when compared to the size of the nuclei. The phenomenological diffuse interface theory tries to improve the droplet model by taking into account of the interface between solid–liquid, liquid–vapor systems which actually extends to several molecular layers in contrast to the assumption of a sharp interface of the classical droplet model. The DIT considers a strongly curvature-dependent surface tension related to a characteristic interface thickness. The model takes into account of the bulk solid and liquid values of enthalpy and entropy within the interface region.

6. Nonclassical Nucleation Pathways

Modern experimental techniques have shown that the nucleation process in solution crystallization proceeds through intermediate stages before reaching a thermodynamically stable phase. Complex materials like proteins, colloids, minerals, and polymeric solutions show that this behavior can be interpreted in terms of the rule of stages. Oswald's rule of stages states that in the course of transformation of an unstable or metastable system into a stable one, the system does not go directly to the most stable conformation, but prefers to reach intermediate stages having closest free energy to the initial state.

6-1. Observation of Two-step mechanism in Colloidal model system

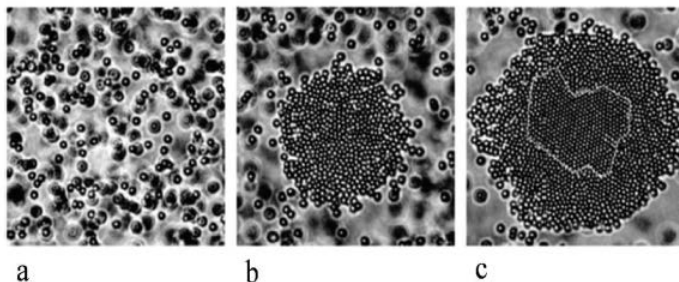


Figure 11. Nonclassical pathway to nucleation in the colloidal model system (polystyrene particles of diameter $0.99 \mu\text{m}$) via amorphous dense phase (a) dilute mother phase (b) 2D amorphous dense droplets formed on glass surface (c) crystal nucleation from amorphous phase. (Reproduced with permission from ref 112. Copyright 2007 American Chemical Society.)

Colloidal particles are used as model systems to study the nucleation process due to their larger size, ease of characterization due to slow diffusion in liquids, and the tunability of interactions. Theoretical and experimental evidence has shown that the nucleation is mediated by the dense liquid precursor phases, and this has been tested in colloidal systems.

6-2~6-5. Evidence of two-step mechanism or metastable phases

6-6. Nucleation in solid-solid phase transitions

6-7. Metastable phases in the freezing of Ice

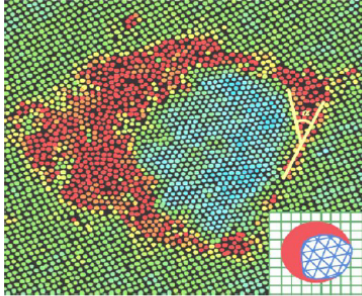


Figure 15. Transition from 5 layer square (\square) lattice to 4 layer triangular (Δ) lattice structure in s-s transition is shown as an example for two-step nucleation via the formation of an intermediate liquid phase. The parent \square phase is shown in green, liquid like nucleus is shown in red, and the evolving Δ phase is shown in blue inside the liquid phase. The contact angle α of Δ lattice at the junction of \square - Δ -liquid as shown in the inset is less than 90° and it does not wet the square lattice. (Reproduced with the permission from ref 150. Copyright 2014 Nature Publishing Group.)

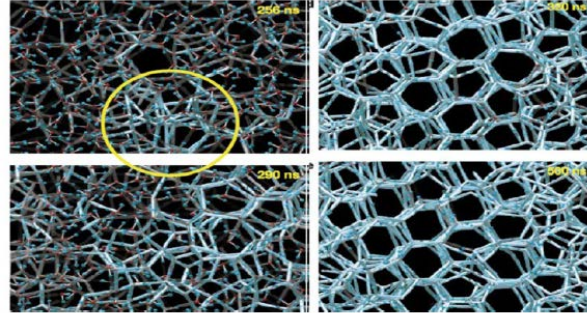


Figure 16. Molecular trajectories showing the phase transition from pure water to ice. The encircled region shows the polyhedral nucleus composed of hydrogen bonds formed spontaneously at $t = 256$ ns; at $t = 290$ ns, the nucleus expands in 3D space leading to six membered rings; images at $t = 320$ ns and 500 ns show the rapid growth of stacked honeycomb structure throughout the system. (Reproduced with the permission from ref 153, Copyright 2002 Nature Publishing Group.)

CONCLUSION

The basic theories underlying nucleation and the evidence to support them have been reviewed. From the comparison of nucleation in different systems, it can be inferred that although CNT offers a platform to start with, more sophisticated models to capture the complexity of molecular level events accompanying nucleation are required. It appears that classical theory depicts one of the possible available pathways available to nucleation. The probability of a system to choose a direct/indirect pathway is difficult to predict with the present understanding, since the complicated kinetics and the various factors governing the formation of metastable clusters poses a major hurdle in the theoretical treatments. The future works have to focus on the governing kinetics of formation of crystals from clusters to extract more information on the controlling mechanisms. Kinetic and thermodynamic treatments would be more complicated for the system when direct and indirect pathways coexist or if it nucleates in a classical way in spite of the existence of intermediate metastable states or the dominance of single metastable component in the systems with multiple metastable components. Though the initial phase in the evolution of the nonclassical pathway has indicated complex possible routes, a much large theoretical and experimental foundation is needed to clearly ascertain the role of intermediates and to gain control over the nucleation phenomena.