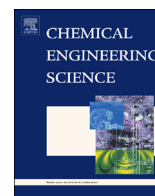




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## Dispersions in crystal nucleation and growth rates: Implications of fluctuation in supersaturation

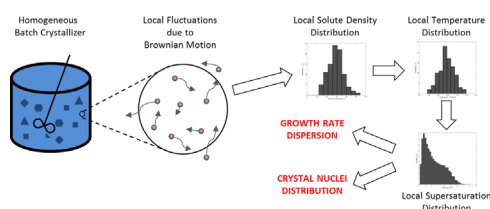
Meenesh R. Singh, Doraiswami Ramkrishna\*

School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, USA

## HIGHLIGHTS

- Stochastic model for supersaturation fluctuations.
- Modeling of dispersions in crystal nucleation and growth rates.
- Predicted morphology distribution for KAP crystal nuclei.
- Experimental validation of predicted growth rate dispersions in KAP crystals.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Crystallization is one of the most commonly used and relatively well explored techniques in industries. Yet there are beleaguering issues towards fundamental understanding of this process. One of the curious observations is the appearance of unavoidable dispersions in nucleation and growth rates of crystalline materials grown under homogenous bulk conditions. These dispersions can contribute significantly towards polydispersity in crystalline products. The classical models such as Gibbs critical nucleation theory and Burton–Cabrera–Frank growth models primarily relate nucleation and growth to supersaturation. Therefore, the dispersions in nucleation and growth rates can be related to the local fluctuations in supersaturation. These local fluctuations are driven by the Brownian motion of solute molecules which affects the local concentration and temperature and hence supersaturation. This article presents a stochastic model to describe fluctuations in supersaturation and thereby dispersions in crystalline materials. The stochastic model is derived from the framework of density and temperature fluctuations. The resulting dispersions in size and shape of nuclei are obtained by multi-dimensional maximization of Gibbs free energy in morphology domain of potassium acid phthalate. The model predictions are validated with the experimental measurements of growth rate dispersions in potassium acid phthalate crystals. The proposed framework provides the first *ab initio* predictions for the observed dispersions in crystallization processes.

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## 1. Introduction

The advanced techniques to predict (Singh and Ramkrishna, 2013; Singh et al., 2013) and measure (Singh et al., 2012) crystal morphologies and face-specific growth rates have contributed significantly to the understanding of crystallization. The underlying processes of crystallization such as nucleation and growth are known to affect sizes and morphologies of crystals. The

solution crystallization is primarily driven by the supersaturation which is often quantified as the solute concentration relative to its saturation limit. The existing theories of crystal nucleation and growth provide a deterministic relationship of the size and morphology of crystals with the supersaturation (Myerson, 2002). Therefore it is quite natural to expect that under fixed crystallization conditions, including supersaturation, crystals will nucleate of mono-dispersed sizes and morphologies that will grow identically, which are often contrary to the experimental observations. Such evolution of a population of crystals is usually described by hyperbolic population balance equations with Dirac

\* Corresponding Author. Tel.: +1 765 494 4066; fax: +1 765 494 0805.

E-mail address: [ramkrish@purdue.edu](mailto:ramkrish@purdue.edu) (D. Ramkrishna).

delta type forcing function or boundary condition. Clearly, the solutions of such population balance equations at fixed operating conditions should follow a uniform distribution. [Randolph and White \(1977\)](#) showed that the spreading of size distribution is due to random fluctuations in growth rates. The synthesis of nanoparticles in micellar solutions is a good example of batch crystallization where breakage and aggregation are negligible, and the only processes governing their sizes and morphologies are nucleation and growth ([Taleb et al., 1997](#)). Non-uniform size and morphology distributions in crystalline materials growing under fixed conditions are commonly observed and so far they have been dealt with empirically in the literature ([Randolph and Larson, 1971](#)). This article presents an *ab initio* approach to explain such dispersions in nucleation and growth rates occurring in crystallization, based on the fundamentals of Brownian dynamics.

Growth rate dispersion is defined as the variations in growth rates under fixed thermodynamic and hydrodynamic conditions, including supersaturation. Crystalline materials can show wide range of dispersion in growth rates based on the environmental conditions. Experimental values of growth rate dispersion for different crystalline materials can be found in review articles ([Garside, 1985](#); [Ulrich, 1989](#)). The growth of crystals or their faces is due to transfer of solute molecules from bulk to the kink sites on the crystal faces. The growth rates are therefore dependent on the mechanism of kink site formation and the supersaturation of solute molecules, both of which can be stochastic. The densities of kink sites and their evolution are functions of temperature and supersaturation. In general, the growth rates functions ([Winn and Doherty, 2000](#)) can be expressed as

$$\dot{H}_i = g(\phi_i^{\text{kink}}, T)f(S) \quad (1)$$

where  $\dot{H}_i$  is a growth rate of *i*th face,  $\phi_i^{\text{kink}}$  the free energy of kink,  $T$  is the temperature and  $S$  is supersaturation defined as ratio of solute concentration to the saturation concentration. Eq. (1) indicates that the growth rates are functions of thermodynamic properties that determine  $\phi_i^{\text{kink}}$  and the dynamic conditions such as temperature and supersaturation. The dynamic conditions are the manifestation of Brownian motion of molecules which on a smaller length scale tend to fluctuate. That means, even if the bulk temperature and supersaturation of the crystallizer are fixed they are bound to fluctuate locally due to Brownian motion. Such fluctuations tend to dissipate with increase in length scale. The growth rates are the realization of the progression of kink sites whose length scales are small enough to observe significantly larger fluctuations. The calculations of growth rate dispersion are predicated on the assumption that Eq. (1) may be applied on a time scale in which temperature and supersaturation fluctuate.

Nucleation is another local phenomenon that is primarily driven by supersaturation. The Gibbs critical nucleation theory relates the equilibrium size and shape of crystal nuclei with supersaturation and temperature ([Myerson, 2002](#)). Furthermore, the rate of nucleation derived from the Arrhenius law also shows the direct dependence on supersaturation and temperature. In this case, the Brownian motion induced fluctuations in supersaturation and temperature will yield distributions in size and shape of nuclei and the nucleation rates. Calculations of growth rate dispersion, nuclei size and shape distributions and nucleation rate distribution resulting from local fluctuations are shown for potassium acid phthalate crystals.

This article is organized as follows. In [Section 2](#), we present a broad outline of the theory which features its salient implements deferring mathematical details of their development to suitably organized Appendices. [Section 3](#) predicts the nuclei morphology distribution from the distribution of supersaturation using Gibbs critical nucleation theory. [Section 4](#) uses the experimentally measured face-specific growth rate functions of Potassium Acid

Phthalate to predict the growth rate dispersion. [Section 5](#) implements the identified growth rate dispersion and nucleation kernels to population balance equations. [Section 6](#) gives the summary of work with the scope for future extension.

## 2. Theory

As articulated earlier, our goal is to develop a theory by which experimentally observed dispersion in nucleation and growth rates can be predicted. The theory is built on attributing this observed dispersion to the fluctuations in number density of solute molecules and temperature due to Brownian motion. We start from the usual premise that the supersaturation drives nucleation and growth in crystallization. Supersaturation, defined as the concentration of solute relative to the saturation concentration, can be expressed in many ways. One of the ways to describe supersaturation  $S$  is

$$S = \frac{c}{c_{\text{sat}}[T]} \quad (2)$$

where  $c$  is the molar concentration and  $c_{\text{sat}}$  is the saturation concentration which is a function of temperature  $T$ . Predicting the effects of other environmental factors such as co-solvents, additives, pressure, electromagnetic field and sonication on fluctuations in saturation concentration requires more sophisticated theory which is outside the scope of this article. The temperature-dependent saturation concentration is the most common scenario in solution-based crystallization and thus relating supersaturation to number density of solute molecules and temperature.

The total number  $n$  of solute molecules in an infinitesimal volume  $v$  tends to fluctuate about the bulk concentration due to Brownian motion. The fluctuations in the number density  $c$  of solute govern the fluctuations in mean-square-speed of molecules and hence temperature in the infinitesimal volume. Therefore, the fluctuations in the supersaturation in a small volume  $v$  can be written as

$$S(t) = \frac{n(t)}{vc_{\text{sat}}[T(t)]} \quad (3)$$

The magnitude of fluctuations is inversely proportional to the control volume  $v$ . Identification of characteristic length scales of nucleation and growth are therefore important for accurate predictions of dispersion. For example, the critical length scale of nucleation can be obtained from Gibbs critical nucleation theory and that of growth is governed by the underlying mechanisms such as spiral growth, 2D nucleation and surface roughening. The critical length scales will set the control volume to predict fluctuations in number  $n(t)$  and temperature  $T(t)$  whose theories will be discussed in [Sections 2.1](#) and [2.2](#), respectively.

### 2.1. Density fluctuations

The framework of density fluctuations due to Brownian motion of solute molecules in an infinitesimal volume is developed from the dynamic exchange of molecules between the system and surrounding. Such exchange of molecules in a system of infinitesimal volume  $v$  inside a very large volume  $V$  containing  $N$  solute molecules yields an equilibrium distribution. [Appendix A](#) shows that the equilibrium distribution of the number  $n$  of solute molecules, uniformly spreads under Brownian motion, follows Poisson distribution.

$$P_n(n) = \frac{\bar{n}^n e^{-\bar{n}}}{n!} \quad (4)$$

whose mean and variance are equal to the average number of molecules  $\bar{n}$  in the volume  $v$ . ([Chandrasekhar, 1943](#)) This

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