



# Homogeneous crystal nucleation in Ni droplets



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## ABSTRACT

Crystal nucleation kinetics is often represented by induction times or metastable zone widths (Kulkarni et al., 2013; Bokeloh et al., 2011). Repeating measurements of supercooling or time delay, at which phase transition is detected, are statistically processed to determine the so-called survivorship function, from which nucleation rate is computed. The size distribution of nuclei is difficult to measure near the critical size directly, and it is not clear which amount of nuclei is formed at the moment when the phase transition is detected. In the present paper, kinetic nucleation equations are solved for the crystal nucleation in Ni liquid droplet to determine the number of nuclei formed within a considered system. Analysis of supercooling experimental data, based on the classical nucleation theory (CNT), computes appropriate values of the nucleation rate. However, CNT underestimates the number of nuclei ( $F \ll 1$  for supercritical sizes). Taking into account the dependence of the surface energy on nucleus size to data analysis overcomes this discrepancy and leads to reasonable values of the size distribution of nuclei.

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## 1. Introduction

Formation of crystal nuclei occurs in supercooled (or supersaturated) parent phase due to sufficiently large fluctuations. Small clusters have a tendency to diminish, and supercritical clusters (nuclei of a new phase) grow up to microscopic sizes. During this process, it is necessary to overcome a so-called nucleation energy barrier. It is frequently difficult to recognize if the formation of nuclei occurs by homogeneous or heterogeneous nucleation or by both processes together. Nuclei form generally on some heterogeneities whose origin is often unknown, and their distribution is rather random.

Turnbull [1] measured supersaturation of supercooled liquid mercury droplets to suppress heterogeneous nucleation. In sufficiently small volumes the stochastic nature of crystal nucleation was observed by induction times and metastable zone widths (MSZW) measurements [2–5]. Kulkarni et al. [2] used both of these methods to study crystal nucleation kinetics of isonicotinamide in ethanol. Statistical evaluation of crystallization behavior was obtained from repeating experiments. Induction time measurements at constant temperature showed significant variation for equally supersaturated samples. The cumulative probability distribution function was computed from experimental data of induction times. Supercooling, at which phase transition occurred, was

measured by MSZW method at various cooling rates to determine (similarly as for induction time measurements) the cumulative probability distribution function, from which the stationary nucleation rate was computed. The induction time of nucleation was related to the moment when light transmission decreased because of formation of crystals in solution. Lenka and Sarkar [3] studied the metastable zone width and induction time for crystallization of L-asparaginohydrate. These measurements revealed a homogeneous nucleation region at high supersaturations and a heterogeneous nucleation region at low supersaturations. Brandel and ter Horst [4] measured induction time distribution under equal conditions in 1 ml racemic diprophylline solution to determine heterogeneous nucleation rates in two solvents. Shiau [6] showed that pre-exponential factor and interfacial energy calculated from the MSZW data, using the integral method, and from the induction data, using the conventional method, are consistent. Bokeloh et al. [5] studied crystallization in Ni droplets (from 23  $\mu\text{g}$  to 63 mg mass) by a combination of differential scanning calorimetry (DSC) experiments and Monte Carlo (MC) simulation. Repeating measurements of the undercooling  $\Delta T$ , at which crystallization was detected at continuous cooling, enable to compute the so-called survivorship function  $P_{sur}(\Delta T)$  (identical with probability distribution function). DSC measurements of crystallization in Ni droplets with various masses allow to determine the nucleation rate,  $J$ , (i.e. the number of nuclei formed in unit volume per unit time) from [5]

$$P_{sur}(\Delta T) = 1 - \exp\left(-\int J(\Delta T)Vdt\right) \quad (1)$$

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over 8 orders of magnitude, where  $V$  denotes the droplet volume. Wang et al. [7] studied homogeneous nucleation and growth in supercooled liquid Cu via X-ray diffraction, resp. molecular dynamics simulations. It is concluded that microstructure of formed crystallites depends on thermal fluctuations and supercooling, respectively.

MSZW and induction time measurements methods are frequently used to determine the stationary nucleation rate in the course of crystallization in a liquid phase. However, one has no information about the size distribution of crystallites. The aim of this work is to determine the number of nuclei as a function of time for homogeneous nucleation and growth in Ni liquid droplets.

## 2. Model

Homogeneous crystal nucleation in Ni droplet is considered within context of the classical nucleation theory (CNT). The number of nuclei,  $F_i(t)$ , consisting of  $i$  atoms within unit volume at time  $t$  is governed by the following equation [8,9]:

$$\frac{dF_i(t)}{dt} = J_{i-1} - J_i, \quad (2)$$

where

$$J_i(t) = k_i^+ F_i - k_{i+1}^- F_{i+1} \quad (3)$$

is the nucleation rate (i.e. the number of  $i$ -sized nuclei formed in unit volume at time  $t$ ) and  $k_i^+$  ( $k_i^-$ ) denotes the attachment (detachment) frequency.

The attachment frequency in condensed systems was introduced by Turnbull and Fisher [10] as follows:

$$k_i^+ = \varrho_s A_i \left( \frac{k_B T}{h} \right) \exp \left( -\frac{E}{k_B T} \right) \exp \left( -\frac{q \Delta g_i}{k_B T} \right), \quad (4)$$

where  $\varrho_s$  denotes the number density of nucleation sites on the nucleus surface,

$$A_i = \gamma i^{2/3} \quad (5)$$

is the surface area of nucleus,  $E$  stands for the activation energy of diffusion across the phase interface,  $k_B$  and  $h$  denote the Boltzmann and Planck constants,  $T$  is temperature,

$$\Delta g_i = W_{i+1} - W_i, \quad (6)$$

and the work of formation of clusters using the capillarity approximation can be expressed by [11]:

$$W_i = -i \Delta \mu + A_i \sigma. \quad (7)$$

Above,

$$q = 0.5[1 + \text{sign}(\Delta g_i)] \quad (8)$$

and  $\sigma$  is the surface energy of nucleus. The critical size,  $i^*$ , corresponds to the size, when  $W_i$  reaches maximum and thus one gets (from condition for extremum,  $dW_i/dt = 0$ ):

$$i^* = \left( \frac{2\gamma\sigma}{3\Delta\mu} \right)^3. \quad (9)$$

Subcritical nuclei ( $i < i^*$ ) have tendency to dissolve ( $k_i^+ < k_i^-$ ) and supercritical nuclei are growable ( $k_i^+ > k_i^-$ ). At the critical size, both transient frequencies are equal.

Similarly as in [5] the spherical nucleus shape was considered and thus the following relationship between nucleus radius  $r$  and the number of nuclei within nucleus hold:

$$\frac{4}{3}\pi r^3 \varrho_C = i m_1, \quad (10)$$

where  $m_1$  is the atom mass,  $\varrho_C$  is the density of crystalline phase and, consequently [see Eq. (5)],

$$\gamma = \sqrt[3]{36\pi} \left( \frac{m_1}{\varrho_C} \right)^{2/3}. \quad (11)$$

The detachment frequency can be determined from the local equilibrium principle (when  $J_i = 0$ ):

$$k_i^+ F_i^0 = k_{i+1}^- F_{i+1}^0, \quad (12)$$

where

$$F_i^0 = N_1 \exp \left( \frac{W_i}{k_B T} \right) \exp \left( -\frac{W_i}{k_B T} \right) \quad (13)$$

corresponds to the equilibrium distribution of nuclei and  $N_1$  is the number of atoms in supercooled liquid droplet.

The difference in the chemical potential between both phases can be approached by:

$$\Delta\mu = \frac{\Delta h_E (T_E - T)}{N_A T_E}, \quad (14)$$

where  $\Delta h_E$  is the heat of fusion,  $T_E$  denotes the melting temperature and  $N_A$  is the Avogadro constant.

Under assumption that the number of atoms in the parent phase does not change in time the stationary state is reached after a certain induction time, i.e.  $J_i = J^S = \text{const}$ . The stationary nucleation rate is then determined by [8]:

$$J^S = \left( \sum_{k=1}^{\infty} \frac{1}{k_i^+ F_i^0} \right)^{-1}. \quad (15)$$

For numerical solution of kinetic equations, it is appropriate to take the initial size distribution equal to the equilibrium one up to cluster size  $i_0$  [12]:

$$F_i(t=0) = F_i^0 \quad \text{for } i \leq i_0, \quad (16)$$

$$F_i(t=0) = 0 \quad \text{for } i > i_0. \quad (17)$$

The total number of atoms within system is given by:

$$N_T = \sum_{i=1}^{i_0} i F_i^0. \quad (18)$$

In small confined systems depletion of atoms during the phase transition occurs [9,11], i.e., the number of atoms in liquid droplet decreases with time:

$$F_1(t) = N_T - \sum_{i>1} i F_i(t). \quad (19)$$

CNT enables to determine stationary nucleation rate [see Eq. (15)] under the assumption that the number of atoms within parent phase remains unchanged, i.e. the following condition is used:

$$F_1(t) = F_1(0). \quad (20)$$

Applying Eq. (19) allows to check  $N_T \gg \sum_{i>1} i F_i(t)$  condition, which is crucial for CNT model.

Numerical computation finishes when a certain maximum cluster size,  $l$ , is reached.

## 3. Results and discussion

As a model system, crystal homogeneous nucleation in Ni droplets is studied. Bokeloh et al. [5] determined from repeating DSC measurements of undercooling of Ni liquid droplet the stationary nucleation rate,  $J^S$ , from the survivorship function  $P_{sur}$  – see Eq. (1). Input parameters for numerical computation:  $\varrho_C = 8357 \text{ kg m}^{-3}$ ,

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