

Size distribution and growth rate of crystal nuclei near critical undercooling in small volumes

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Abstract. Kinetic equations are numerically solved within standard nucleation model to determine the size distribution of nuclei in small volumes near critical undercooling. Critical undercooling, when first nuclei are detected within the system, depends on the droplet volume. The size distribution of nuclei reaches the stationary value after some time delay and decreases with nucleus size. Only a certain maximum size of nuclei is reached in small volumes near critical undercooling. As a model system, we selected recently studied nucleation in Ni droplet [J. Bokeloh et al., Phys. Rev. Let. 107 (2011) 145701] due to available experimental and simulation data. However, using these data for sample masses from 23 μg up to 63 mg (corresponding to experiments) leads to the size distribution of nuclei, when no critical nuclei in Ni droplet are formed (the number of critical nuclei < 1). If one takes into account the size dependence of the interfacial energy, the size distribution of nuclei increases to reasonable values. In lower volumes ($V \leq 10^{-9} \text{ m}^3$) nucleus size reaches some maximum extreme size, which quickly increases with undercooling. Supercritical clusters continue their growth only if the number of critical nuclei is sufficiently high.

1. Introduction

Nucleation (homogeneous or heterogeneous) is the initial process leading to the formation of a new phase when a certain nucleation energy barrier is overcome. In the case of homogeneous nucleation nuclei of a new phase are formed at any monomer (atom or molecule) within parent phase while at heterogeneous nucleation the nuclei are created on foreign surfaces, impurities, surface defects, etc. A special case of heterogeneous nucleation is formation of nuclei on active centers [1-3], when its probability on these centers is higher. Nucleation plays a decisive role in determining the crystal structure and the size distribution of nuclei. A better understanding of nucleation opens the possibilities to new approaches to control of crystallization process.

Critical undercooling (corresponding to situation when a detectable amount of thermodynamically stable phase is formed), induction time, and metastable zone width provide important information about nucleation process. From the viewpoint of nucleation theory the computation of the critical undercooling (resp. supersaturation for the formation of droplets from vapor or crystals from solution) is based on assumption that the stationary nucleation rate reaches a certain concrete value [4]. Alternatively, the critical supersaturation can be derived from the condition that one supernucleus of preset number of molecules (or atoms) is formed in a parent phase [5, 6].

Repeated measurement of the critical undercooling showed that nucleation is a stochastic process [7, 8]. If one supposes Poisson distribution of nuclei [9-11], the nucleation rate and the work of



formation of nuclei can be derived from the survivorship function defined as the fraction of experiments in which crystallization did not yet occur at a given value of undercooling ΔT . Recently, Bokeloh et al. [7, 12] analyzed the differential scanning calorimetry (DSC) experiments to determine nucleation rate and the work of formation of nuclei in Ni droplets together with the Monte Carlo (MC) simulations. In DSC experiments the released latent heat is detected. However, one has no information about the size distribution of nuclei and the maximum size of nuclei formed within nucleating system.

The aim of this paper is to extend aforementioned research to determine the size distribution of nuclei by numerical solution of kinetic equations in small Ni droplets (for which all input data are known) and to show how small changes in critical undercooling influence the maximum size of formed nuclei.

2. Model

Homogeneous nucleation in Ni droplets is considered within context of the standard nucleation theory. The number of nuclei, $F_i(t)$, formed by i atoms at time t is governed by the following equation [13]:

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

where

$$J_i(t) = k_i^+ F_i - k_{i+1}^- F_{i+1} \quad (2)$$

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 [4]:

$$k_i^+ = \rho_s A_i \left(\frac{k_B T}{h} \right) \exp\left(-\frac{E}{k_B T}\right) \exp\left(-\frac{q \Delta g_i}{k_B T}\right), \quad (3)$$

where ρ_s denotes the number density of nucleation sites on the nucleus surface,

$$A_i = \gamma i^{2/3} \quad (4)$$

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,

$$\Delta g_i = W_{i+1} - W_i, \quad (5)$$

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

$$W_i = -i\Delta\mu + A_i\sigma. \quad (6)$$

Above,

$$q = 0.5[1 + \text{sign}(\Delta g_i)] \quad (7)$$

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

$$i^* = \left(\frac{2\gamma\sigma}{3\Delta\mu} \right)^3. \quad (8)$$

Subcritical nuclei ($i < i^*$) have tendency to dissolve ($k_i^+ < k_i^-$) and supercritical nuclei have tendency to growth ($k_i^+ > k_i^-$). At the critical size both transient frequencies reach the same value (metastable equilibrium).

Molecular simulations [15, 16] showed that σ increases with i . Tolman [17] derived the following equation:

$$\sigma(i) = \sigma_\infty(1 - 2\delta/r) \quad (9)$$

for the size dependence of σ , where σ_∞ denotes the interfacial energy in the limit of flat interface. However, this dependence varies greatly with the applied value of the Tolman length δ . Merikanto et al. [15] derived the following approximation for Lenard-Jones clusters:

$$\sigma(i) \approx \sigma_\infty - \frac{A_1 \sigma_\infty + 13.6 k_B T}{A_i} \quad (10)$$

where no parameter δ is needed.

Similarly as Bokeloh et al. [7] the spherical nucleus shape was considered and thus the following relationship between nucleus radius r and the number of nuclei within nucleus holds:

$$\frac{4}{3} \pi r^3 \rho_C = i m_1, \quad (11)$$

where m_1 is the molecular mass and ρ_C is the density of crystalline phase and, consequently [see Eq. (4)],

$$\gamma = \sqrt[3]{36\pi} \left(\frac{m_1}{\rho_C} \right)^{2/3}. \quad (12)$$

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

$$k_i^+ F_i^0 = k_{i+1}^- F_{i+1}^0, \quad (13)$$

where

$$F_i^0 = N_1 \exp\left(\frac{W_i}{k_B T}\right) \exp\left(-\frac{W_i}{k_B T}\right) \quad (14)$$

denotes the equilibrium distribution of nuclei, N_1 is the number of atoms in undercooled melt.

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

$$\Delta\mu = \frac{\Delta h_E (T_E - T)}{N_A T_E}, \quad (15)$$

where Δh_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, when $J_i = J^S = \text{const}$. The stationary nucleation rate is determined by [13]:

$$J^S = \left(\sum_{i=1}^{\infty} \frac{1}{k_i^+ F_i^0} \right)^{-1}. \quad (16)$$

The growth rate of nuclei can be computed from the transient frequencies:

$$v = \frac{dr}{di} \frac{di}{dt} = \frac{dr}{dt} (k_i^+ - k_{i+1}^-) \quad (17)$$

and in the limit of flat surface ($i \rightarrow \infty$) one gets:

$$v_\infty = \frac{1}{3} \rho_S \left(\frac{k_B T}{h} \right) \exp\left(-\frac{E}{k_B T}\right) \left(\frac{3m_1}{4\pi\rho_C} \right)^{1/3} \left[1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right) \right]. \quad (18)$$

Growth rate v , determined according to Eq. (17), leads to a negative values for subcritical sizes. Alternatively, one can determine the growth rate from the size of the largest nucleus $i_{\max}$ [respectively $r_{\max}$ from Eq. (11)] formed within volume V at time t , when

$$F_i(t) V = 1 \quad (19)$$

and thus $i_{\max}(t)$ [respectively $r_{\max}(t)$] dependence is determined.

For numerical solution of kinetic equations, the following initial conditions will be used:

$$F_i(t=0) = F_i^0 \quad \text{for } i \leq i_0 \quad (20)$$

$$F_i(t=0) = 0 \quad \text{for } i > i_0, \quad (21)$$

$$F_1(t) = N_T - \sum_{i=2}^l F_i(t), \quad (22)$$

$$F_l(t) = 0, \quad (23)$$

where l denotes the largest size of nuclei considered in the computation and

$$N_T = N_1 + \sum_{i=2}^{i_0} i F_i^0 \quad (24)$$

is the total number of atoms in nucleating system. Eq. (22) takes into account decrease of atoms within parent phase. Classical nucleation theory (CNT) suppose that the number of atoms within parent phase does not change, i. e. the following condition is used:

$$F_1(t) = N_1. \quad (25)$$

3. Results and discussion

As a model system, homogeneous nucleation in Ni droplets was chosen. Following accessible experimental data and also input parameters for standard model are used: $\Delta h_E = 17.29 \text{ kJ mol}^{-1}$, $T_E = 1748 \text{ K}$, $\rho_C = 8357 \text{ kg m}^{-3}$ and $\sigma = (\sigma_m T/T_E)$, where $\sigma_m = 0.275 \text{ J m}^{-2}$ [7]. We numerically solved Eq. (1) for maximum size of nuclei $l = 250000$ [see Eq. (23)] to determine the size distribution of nuclei, $F_i(t)$, at undercooling $\Delta T = (T_E - T) = 300 \text{ K}$ (corresponding to critical size $i^* = 450$) supposing size-independent interfacial energy – see Figure 2 in [18]. The number of critical nuclei at the stationary state $F_{450}^S \approx 4 \times 10^5 \text{ m}^{-3}$ and one gets for the volume, in which one nucleus is formed, $V_1 = 1/F_i^S = 2.5 \times 10^{-6} \text{ m}^3$. Critical supersaturation was measured for Ni sample masses from $23 \mu\text{g}$ up to 64 mg [7] which corresponds to sample volumes $V = 2.9 \times 10^{-12} \text{ m}^3 - 7.15 \times 10^{-9} \text{ m}^3$ (i. e. much less than V_1). No critical nuclei are formed according to the standard nucleation theory in the difference of experimental data. That is why we have taken into account the size dependence of the interfacial energy (Figure 1) similarly as in our previous work [18]. However, for small cluster sizes (subcritical nuclei) the $\sigma(i)$ gives negative values for Eq. (10) [dotted line in Figure 1] and also for Eq. (9) with $\delta = 1.5 \text{ \AA}$ (dashed line). In further numerical computations $\sigma(i)$ dependence was taken using Eq. (9) with $\delta = 0.8 \text{ \AA}$ (full line), for which $\sigma(i) > 0$ for any i .

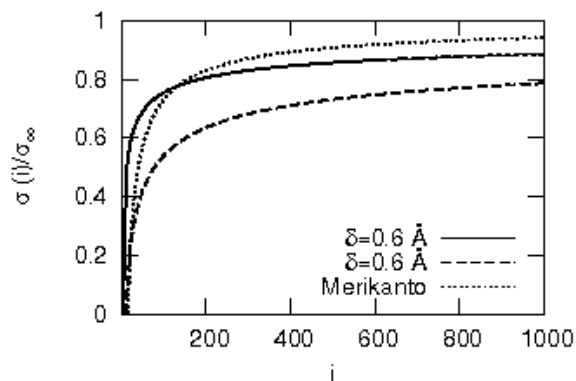


Figure 1. The interfacial energy $\sigma(i)$ scaled by the flat interface limit σ_∞ as a function of cluster size i using Eq. (10) [dotted line] and Eq. (9) with $\delta = 1.5 \text{ \AA}$ (dashed line) and $0.8 \text{ \AA}$ (full line).

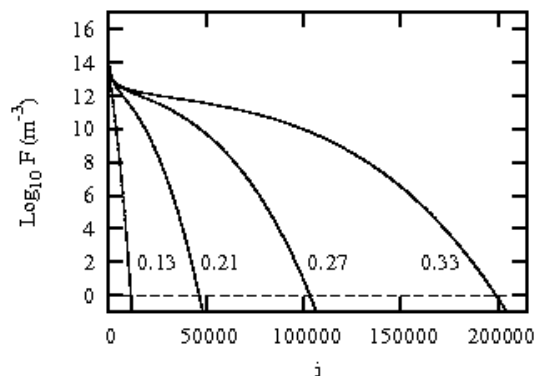


Figure 2. The size distribution of nuclei, F , as a function of cluster size, i , at undercooling $\Delta T = 300 \text{ K}$ for time $t = 0.13, 0.21, 0.27$ and 0.33 s . Dashed line corresponds to $F = 1$.

If one takes into account $\sigma(i)$ dependence according to Eq. (9) with $\delta = 0.8 \text{ \AA}$, after some time delay the stationary number of nuclei at $\Delta T = 300 \text{ K}$ reaches at critical size: $F_{350}^S = 3.2 \times 10^{14} \text{ m}^{-3}$ (experimentally reasonable value). The number of nuclei decreases with nucleus size i and increases with time (Figure 2). It is possible to determine maximum size $i_{\max}$ of nuclei at some preset time t , at which $F_{i_{\max}}(t) = 1$ (dashed line in Figure 2 denotes $F = 1$) and from $i_{\max}(t)$ function the growth rate of nuclei can be determined.

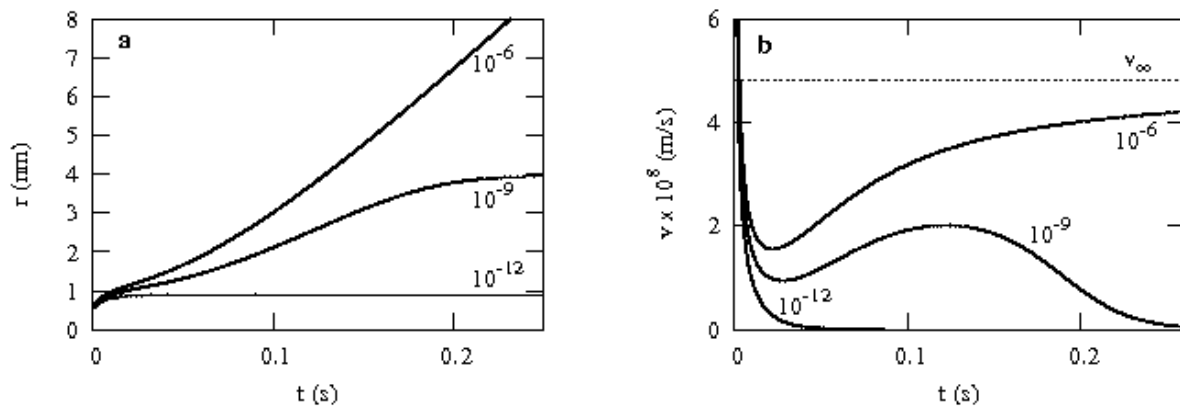


Figure 3. Radius of largest nuclei $r_{\max}$ (a) and growth rates v (b) at undercooling $\Delta T = 300$ K in volumes $V = 10^{-6}$, 10^{-9} , and 10^{-12} m³ as a function of time t .

Radius of the largest nuclei $r_{\max}$ increases with time (at $\Delta T = 300$ K) for larger volumes ($V \geq 10^{-6}$ m³). However, at smaller volumes ($V = 10^{-9}$ and 10^{-12} m³) $r_{\max}$ reaches, at sufficiently long time, some stationary value $r_{\max}^S$, which decreases with lowered volumes (Figure 3a). Moreover, larger nuclei are not formed in the system. The growth rates $v = dr_{\max}/dt$ for a sufficiently short time reach values exceeding the growth rate within a flat interface limit v_∞ and at a certain time decreases to some minimum value, which decreases with system volume (Figure 3b). These minimum values are reached in times corresponding to the time delay of nucleation. In larger volumes ($V \geq 10^{-6}$ m³), the growth rates increase with time close to the flat interface limit v_∞ . In unit volume, size $i_{\max} = 194000$ is attained at time $t = 0.35$ s and longer times would require to solve huge number of equations with increasing CPU computation time. In volume $V = 10^{-9}$ m³ growth rate, after reaching some maximum value at $t = 0.12$ s, goes to zero as the nuclei of maximum size $r_{\max}^S$ are formed.

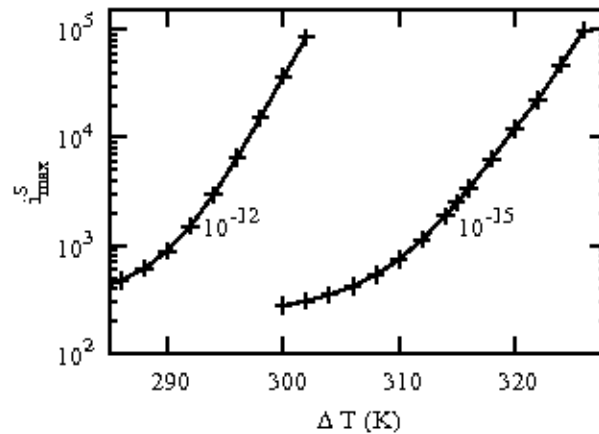


Figure 4. Stationary number of atoms in largest nuclei $i_{\max}^S$ as a function of undercooling $\Delta T = (T_E - T)$ in volumes $V = 10^{-12}$ and 10^{-15} m³. Crosses correspond to supersaturations for which $i_{\max}^S$ was computed.

Finally, we have performed numerical solution of Eq. (1) to show how the maximum size of nuclei is influenced by undercooling near the critical value (Figure 4). At lower undercooling only subcritical nuclei are formed, *e. g.* in volume $V = 10^{-15}$ m³ at undercooling $\Delta T = 300$ K (critical size $i^* = 350$) $i_{\max}^S = 280 < i^*$. It is clear that maximum size of nuclei $i_{\max}^S$ quickly increases with undercooling. At larger volume $V = 10^{-12}$ m³ one needs lower undercooling in comparison with smaller volume $V = 10^{-15}$ m³ to form the same maximum nucleus size.

4. Conclusion

Formation of nuclei near critical supersaturation in Ni small droplets is studied within standard nucleation model. Bokeloh et al. [7] recently presented DSC measurements and also Monte Carlo simulations to determine nucleation rate and the work of formation of nuclei in this system. We calculated the maximum size of nuclei $r_{\max}$ formed in the system from the size distribution of nuclei [condition $F_{r_{\max}}(t) V = 1$] in various volumes V and also growth rate $v = dr_{\max}/dt$ taking into account the size dependence of the interfacial energy. In small volumes a certain maximum size of nuclei $r_{\max}^S$ is reached, which increases with system volumes. The growth rate in larger volumes ($V \geq 10^{-6} \text{ m}^3$) tends to the flat interface limit with increased time. However, in small volumes, as the maximum size $r_{\max}^S$ is reached, the growth rate goes to zero via a certain maximum. The maximum number of molecules in the largest nuclei, $i_{\max}^S$, quickly increases with undercooling and system volume. The growth of supercritical nuclei can proceed only if the number of critical nuclei is sufficiently high in nucleation system.

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