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## Homogeneous nucleation in a Poiseuille flow

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Nucleation in a dynamical environment plays an important role in the synthesis and manufacturing of quantum dots and nanocrystals. In this work, we investigate the effects of fluid flow (low Reynolds number flow) on the homogeneous nucleation in a circular microchannel in the framework of the classical nucleation theory. The contributions of the configuration entropy from the momentum-phase space and the kinetic energy and strain energy of a microcluster are incorporated in the calculation of the change of the Gibbs free energy from a flow state without a microcluster to a flow state with a microcluster. An analytical equation is derived for the determination of the critical nucleus size. Using this analytical equation, an analytical solution of the critical nucleus size for the formation of a critical liquid nucleus is found. For the formation of a critical solid nucleus, the contributions from both the kinetic energy and the strain energy are generally negligible. We perform numerical analysis of the homogeneous nucleation of a sucrose microcluster in a representative volume element of an aqueous solution, which flows through a circular microchannel. The numerical results reveal the decrease of the critical nucleus size and the corresponding work of formation of a critical nucleus with the increase of the distance to axisymmetric axis for the same numbers of solvent atoms and solute atoms/particles.

Keywords: Homogeneous nucleation; Poiseuille flow; Configuration entropy; Critical nucleus size; Work of formation of a critical nucleus.

## 1. Introduction

The rapid growth in nanotechnology has stimulated great interest in synthesizing objects of nanosizes, including nanoparticles<sup>1-3</sup>, quantum dots<sup>4,5</sup>, nanowires<sup>6,7</sup>, nanotubes etc.<sup>8,9</sup>, for the applications in nanoelectronics and nanophotonics. Currently, the fabrication of most quantum dots has been based on the bottom-up approach, which involves nucleation and growth in a dynamic environment, such as in a flow and/or agitation environment<sup>10,11</sup>. The dynamic environment has imposed a challenge to the understanding and analysis of the nucleation and growth behaviors due to the motion of clusters/nuclei/crystals and monomers.

There are reports<sup>12-20</sup> focusing on the analysis of the effect of shear flow and agitation on homogeneous nucleation. Lothe and Pound<sup>12</sup> suggested the need to include the contributions of translational and rotational degrees of freedom in the free energy of formation of clusters in the classical nucleation theory, while their approach led to significant discrepancy between their results and experimental results. Reiss et al.<sup>13</sup> pointed out that careful analysis is needed to avoid the overestimation of molecular configurations and large error in the nucleation rate. Mokshin et al.<sup>14</sup> performed molecular dynamics (MD) simulation for the nucleation of a single-component glass-forming system under shear and incorporated the effect of shear in the effective temperature. They commented that the classical nucleation theory is applicable to uniformly sheared systems. Including the kinetic energy for translational motion and/or rotational motion in the free energy of formation of a state, Reguera and Rubi<sup>15,16</sup> derived the Fokker–Planck equation from mesoscopic nonequilibrium thermodynamics for the growth of clusters in a shear flow and revealed the dependence of the growth and nucleation rates on the flow, as expected. Assuming that both chemical potential difference and interfacial energy are dependent on shear rate, Blaak et al.<sup>21</sup> performed Brownian dynamics simulation for the analysis of the effect of shear on homogeneous nucleation in colloidal suspensions and pointed out the increase of critical nucleus size with the shear rate. However, they did not provide physical basis for the dependence of the chemical potential difference and interfacial energy on the shear rate. Recently, Richard and Speck<sup>22</sup> suggested the need to include the change of interfacial work due to shear-induced deformation in the classical nucleation theory in the analysis of the nucleation in a sheared fluid. They obtained a relation between the pressure difference across the interface between solid and liquid and the flow-induced shear stress in the framework of linear elasticity without introducing surface stress. Their

approach is questionable, since this relation predicts that shear stress can lead to the change of the pressure difference across the interface.

Considering the importance of the synthesis of nano-objects and quantum dots in dynamic environments and the important role of nucleation in controlling the formation of nano-objects and quantum dots, we investigate the nucleation of solute atoms/particles in a fluid/solvent system under Poiseuille flow. The analysis takes into account the contributions of translational and rotational motion and the strain energy stored in clusters and derives an analytical solution of the critical nucleus size for homogeneous nucleation in a flow system.

## 2. Physical Model

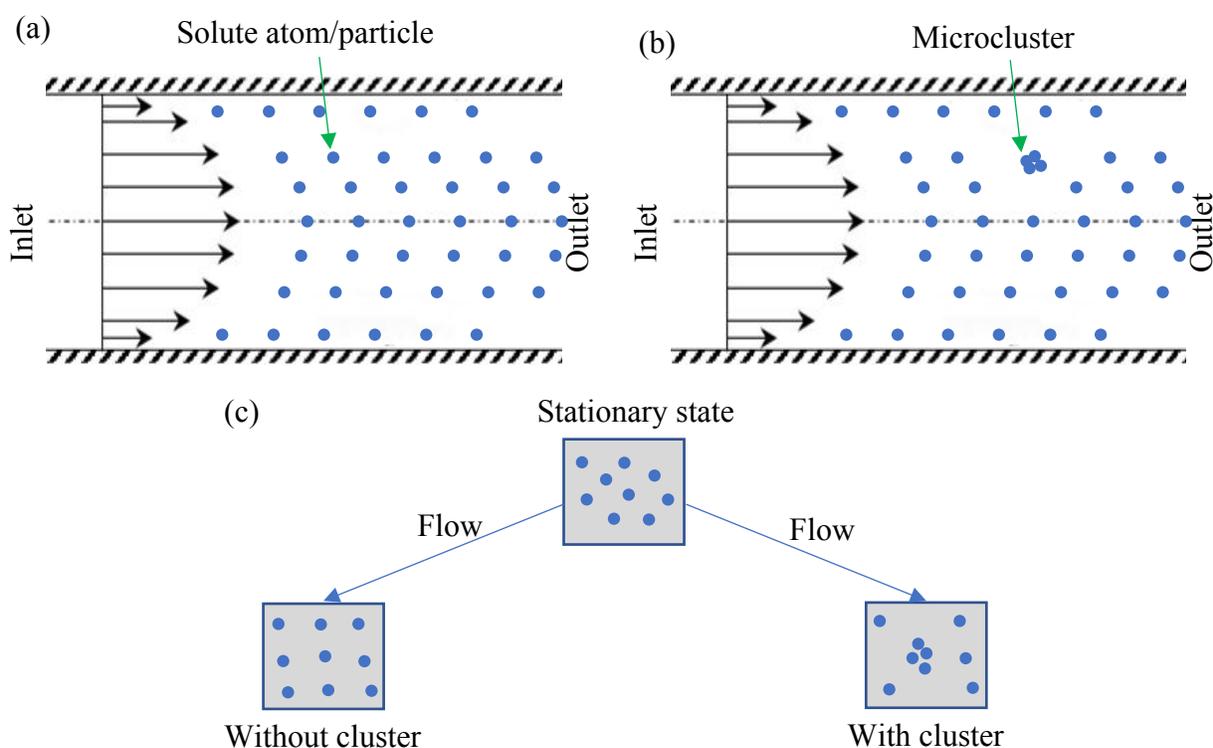


Figure 1. Schematic of a Poiseuille flow with solute atoms/particles dispersed in solvent: (a) without microclusters, (b) with a microcluster, and (c) flow-induced change in local states with and without a microcluster.

Consider a viscous liquid, which consists of solvent and solute atoms/particles. The viscous liquid flows isothermally in a circular channel at steady state, as shown in Fig. 1a, and the nucleation of the solute atoms/particles can occur during the flow (Fig. 1b). Assume that the Reynolds number for the viscous flow is small; there are no formations of vortices during the

flow. For the steady-state flow, we can randomly choose a small volume in the channel as a representative volume element (RVE) (Fig. 1c), in which the numbers of solvent atoms and solute atoms are maintained constant. Note that the RVE size must be small enough macroscopically and large enough microscopically to represent average local behavior.

Let  $N_1$  and  $N_2$  represent the numbers of solvent atoms and solute atoms in the RVE, respectively. Note that the local concentration of solute atoms is dependent on spatial variable and local velocity<sup>23</sup>. The difference of the internal energies of the materials in the RVE between stationary state and a flow state without the formation of microclusters can be calculated as

$$U_1 - U_0 = \sum_{i=1}^{N_1} \frac{1}{2} m_1 V_i^2 + \sum_{i=1}^{N_2} \frac{1}{2} m_2 V_i^2 + N_1(\mu_{f1} - \mu_{s1}) + N_2(\mu_{f2} - \mu_{s2}) \quad (2)$$

where  $U_1$  and  $U_0$  are the internal energies of the materials at the flow state and at the stationary state, respectively,  $m_1$  and  $m_2$  are the atomic masses of the solvent atoms and solute atoms, respectively, and  $V_i$  is the velocity of individual atoms,  $\mu_{f1}$  and  $\mu_{s1}$  are the chemical potentials of the solvent atoms at the flow state and the stationary state, respectively, and  $\mu_{f2}$  and  $\mu_{s2}$  are the chemical potentials of the solute atoms/particles at the flow state and the stationary state, respectively.

Assume that there are no internal degrees of freedom for all the solvent and solute atoms. Under the steady state flow, there are no spatiotemporal evolution of the system (the solvent and solute atoms) in the RVE except local fluctuation the same as the stationary system (Fig. 1c). The thermodynamic state of an atom is determined by its location in the REV and energy (kinetic energy). Thus, the entropy of the system consists of the entropy of mixing,  $S_m$ , the entropy associated with the energy of solvent atoms,  $S_{K1}$ , and the entropy associated with the energy of solute atoms,  $S_{K2}$ , as

$$S = S_m + S_{K1} + S_{K2} \quad (3)$$

Assume that the difference in the entropy of mixing between the stationary state and a flow state without the formation of clusters is negligible. The entropy of mixing,  $S_m$ , can be calculated as<sup>24</sup>

$$S_m = -N_1 k \ln[\gamma_1(1-x)] - N_2 k \ln(\gamma_2 x) \quad (4)$$

with  $k$  being the Boltzmann constant,  $T$  being absolute temperature,  $\gamma_1$  and  $\gamma_2$  being the activity coefficients for the solvent atoms and solute atoms, respectively, and  $x = N_2/(N_1 + N_2)$ . To calculate the entropies associated with the energies of the solvent atoms and solute atoms,  $S_{K1}$  and  $S_{K2}$ , we need to introduce the phase space with coordinates corresponding to the three components of

momentum of atoms <sup>25, 26</sup>. Following the approach given by Bhattacharyya and Dawlaty <sup>26</sup>, the entropies associated with the energies of the solvent atoms and solute atoms,  $S_{K1}$  and  $S_{K2}$ , can be calculated as <sup>25</sup>

$$S_{Ki} = N_i k \ln(N_i I_i) \quad (i = 1, 2) \quad (5)$$

where the effect of the RVE size is neglected. The parameters of  $I_i$  are

$$I_i = \frac{1}{2} m_i \langle V_i^2 \rangle \quad (i = 1, 2) \quad (6)$$

in which  $\langle \bullet \rangle$  represents average value for the solvent/solute atoms in the REV. It is evident that the motion of the solvent atoms and solute atoms in a flow system contributes to the change of the entropy.

Using Eqs. (2)-(5), we obtain the difference of the Gibbs free energies of the materials in the RVE between the stationary state and a flow state without the formation of microclusters as

$$\Delta G_1 = U_1 - U_0 - T\Delta S + P\Delta V \quad (7)$$

$$\begin{aligned} &= \sum_{i=1}^{N_1} \frac{1}{2} m_1 V_i^2 + \sum_{i=1}^{N_2} \frac{1}{2} m_2 V_i^2 + N_1(\mu_{f1} - \mu_{s1}) + N_2(\mu_{f2} - \mu_{s2}) + P\Delta V \\ &\quad - kT [N_1 \ln(N_1 I_1) + N_2 \ln(N_2 I_2)] \end{aligned}$$

in which  $P\Delta V$  represents the work done to the system in the RVE. Note that Eq. (7) is only valid under the condition that the difference in the entropy of mixing between the stationary state and the flow state without the formation of clusters is negligible.

Now, consider the formation of a microcluster in the RVE, as shown in Fig. 1b and 1c. For simplification, we assume that the microcluster is a spherical particle of  $a$  in radius and consists of  $m$  solute atoms. There are  $(N_2 - m)$  solute atoms and a microcluster in the RVE. The difference of the internal energies of the materials in the RVE between the stationary state and a flow state with a cluster is

$$\begin{aligned} U_2 - U_0 &= \sum_{i=1}^{N_1} \frac{1}{2} m_1 V_i^2 + \sum_{i=1}^{N_2-m} \frac{1}{2} m_2 V_i^2 + E_{KC} + E_{SC} + 4\pi\sigma a^2 \\ &\quad + N_1(\mu_{f1} - \mu_{s1}) + (N_2 - m)(\mu_{f2} - \mu_{s2}) + m(\mu_m - \mu_{s2}) \end{aligned} \quad (8)$$

where  $U_2$  is the internal energy of the materials in the RVE at the flow state with a microcluster,  $E_{KC}$  and  $E_{SC}$  are the kinetic energy and strain energy of the microcluster associated with the motion and deformation,  $\sigma$  is the specific interface energy between the microcluster and the liquid in the

RVE, and  $\mu_m$  is the chemical potential per atom in the microcluster at the flow state. For a liquid microcluster, which is referred to as a microcluster that consists of solute atoms, exhibits non-periodic structure and cannot maintain a stationary configuration under shear stress,  $E_{SC} = 0$ . Note that Eq. (8) is based on the assumption that the presence of the microcluster has negligible effect on the flow state of the atoms in the RVE, and the interface energy is a function of local concentration of the solute atoms<sup>24, 27, 28</sup>. The entropy of mixing is

$$S_m = -N_1 k \ln[\gamma_1(1-y)] - (N_2 - m)k \ln(\gamma_2 y) \quad (9)$$

and the entropy associated with the kinetic energy of the solvent and solute atoms,  $S_K$ , is

$$S_K = k [N_1 \ln(N_1 I_1) + (N_2 - m) \ln[(N_2 - m) I_2]] \quad (10)$$

with  $y = (N_2 - m)/(N_1 + N_2 - m)$ .

It is known that the flow of a viscous fluid can cause translational and rotational motion of the particles suspended in the fluid<sup>29</sup>. According to the results given by Jeong and Jang<sup>29</sup>, the translational speed of a microcluster is approximately the same as local fluid speed,  $V_L$ , and the angular speed of a microcluster is approximately linearly proportional to local average fluid speed and the distance to axisymmetric axis for the Poiseuille flow in a circular channel and inversely proportional to the square of the radius of the circular channel,  $r_0$ . Thus, the kinetic energy of the microcluster is

$$E_{KC} = \frac{mm_2}{2} V_L^2 + \frac{mm_2}{5} \alpha^2 V^2 \left( \frac{ar}{r_0^2} \right)^2 \quad (11)$$

in which  $V$  is the average speed of the Poiseuille flow,  $\alpha$  is a proportionality constant between the angular speed and the local average speed, and  $r$  is the distance between the microcluster and the axisymmetric axis.

According to Bretherton<sup>30</sup>, the dependence of the shear stress applied onto the surface of a solid microcluster in a viscous flow is proportional to local fluid speed and inversely proportional to the size of the solid microcluster as

$$\tau \propto \frac{\eta V_L}{a} \quad (12)$$

The strain energy stored in a solid microcluster can be estimated as<sup>22</sup>

$$E_{SC} \approx \frac{4\pi}{3} \frac{\beta a^3}{2G} \left( \frac{\eta V_L}{a} \right)^2 = \frac{2\pi}{3} \frac{\beta a (\eta V_L)^2}{G} \quad (13)$$

Here,  $\eta$  is the viscosity of the viscous fluid,  $\beta$  is a constant, depending on the distribution of the shear stress on the surface of the solid microcluster, and  $G$  is the modulus of the microcluster.

Using the results of (8)-(11) and (13), we obtain the difference of the Gibbs free energies of the materials in the RVE between the stationary state and a flow state with a microcluster as

$$\begin{aligned} \Delta G_2 = & \sum_{i=1}^{N_1} \frac{1}{2} m_1 V_i^2 + \sum_{i=1}^{N_2} \frac{1}{2} m_2 V_i^2 - \sum_{i=1}^m \frac{1}{2} m_2 V_i^2 + \frac{mm_2}{2} V_L^2 + \frac{mm_2}{5} \alpha^2 V^2 \left( \frac{ar}{r_0^2} \right)^2 + P\Delta V \quad (14) \\ & + \frac{2\pi}{3} \frac{\beta a (\eta V_L)^2}{G} + (\mu_m - \mu_{s_2})m + 4\pi\sigma a^2 + kT [N_1 \ln[\gamma_1(1-y)] + N_2 \ln(\gamma_2 y)] \\ & - kT (N_1 \ln[\gamma_1(1-x)] + N_2 \ln(\gamma_2 x)) + N_1 (\mu_{f_1} - \mu_{s_1}) + (N_2 - m)(\mu_{f_2} - \mu_{s_2}) \\ & - kT [N_1 \ln(N_1 I_1) + (N_2 - m) \ln[(N_2 - m) I_2]] \end{aligned}$$

For a small RVE in the Poiseuille flow, we can have  $V_i \approx V_L = 2V[1-(r/r_0)^2]$ . Therefore, the change of the Gibbs free energy of the system in the RVE from the flow state without a microcluster to the flow state with a microcluster is

$$\begin{aligned} \Delta G = \Delta G_2 - \Delta G_1 \quad (15) \\ = \frac{mm_2}{5} \alpha^2 V^2 \left( \frac{ar}{r_0^2} \right)^2 + \frac{8\pi}{3} \frac{\beta a \eta^2 V^2}{G} \left( 1 - \frac{r^2}{r_0^2} \right)^2 + (\mu_m - \mu_{f_2})m + 4\pi\sigma a^2 \\ + kT \left[ N_1 \ln \frac{1-y}{1-x} + (N_2 - m) \ln(\gamma_2 y) - N_2 \ln(\gamma_2 x) \right] \\ - kT \left( N_2 \ln \frac{N_2 - m}{N_2} - m \ln [2(N_2 - m)m_2 V^2 \left( 1 - \frac{r^2}{r_0^2} \right)] \right) \end{aligned}$$

It is evident that there exist contributions from the rotational motion and deformation of the solid microcluster as well as the flow-induced change in the configuration entropy. The effect of the translational motion of the microcluster is negligible due to its small size. The change of the Gibbs free energy is a spatial function of the flow field. Note that the nonslip condition is used in the Poiseuille flow, and the condition of  $r = r_0$  is inapplicable to Eq. (15).

### 3. Critical nucleus number and formation of free energy

For a spherical microcluster of radius  $a$ , the relation between the number of solute atoms,  $m$ , in the microcluster and the radius  $a$  is

$$a = \left( \frac{3m\Omega_2}{4\pi} \right)^{1/3} \quad (16)$$

with  $\Omega_2$  being atomic volume of the solute atoms. According to the theory of thermodynamics, the maximum change of the Gibbs free energy of a system (i.e. zero driving force associated with the interface energy and the change of volumetric Gibbs free energy) determines the state, at which a critical nucleus can be formed, leading to the formation and growth of a crystal. Under the condition of constant pressure and temperature, there is

$$\left. \frac{\partial \Delta G}{\partial a} \right|_{T,P,N_1,N_2} = \left. \frac{\partial \Delta G}{\partial m} \right|_{T,P,N_1,N_2} = 0 \quad (17)$$

Substituting Eq. (15) in Eq. (17) and using Eq. (16), we obtain the critical nucleus number,  $m_c$ , as

$$m_c^{-1/3} = \Delta\Theta_1 + \Delta\Theta_2 - \frac{3}{8\pi\sigma} \left( \frac{3\Omega_2}{4\pi} \right)^{-2/3} \Delta\Theta \quad (18)$$

with the  $\Delta\Theta$ ,  $\Delta\Theta_1$  and  $\Delta\Theta_2$  as

$$\Delta\Theta = \mu_m - \mu_{f2} - kT \ln(\gamma_2 y) \quad (19)$$

$$\Delta\Theta_1 = -\frac{m_c^{2/3} m_2}{8\pi\sigma} \alpha^2 V^2 \left( \frac{r}{r_0^2} \right)^2 - \frac{\beta m_c^{-2/3} \eta^2 V^2}{3\sigma G} \left( 1 - \frac{r^2}{r_0^2} \right)^2 \left( \frac{3\Omega_2}{4\pi} \right)^{-1/3} \quad (20)$$

$$\Delta\Theta_2 = -\frac{3kT}{8\pi\sigma} \left( \frac{3\Omega_2}{4\pi} \right)^{-2/3} \left( 1 + \ln[2(N_2 - m_c)m_2 V^2 \left( 1 - \frac{r^2}{r_0^2} \right)] \right) \quad (21)$$

Here,  $\Delta\Theta$  represents the contribution of the change in the free energy due to the formation of the nucleus at a stationary environment,  $\Delta\Theta_1$  represents the contribution of the kinetic energy and strain energy due to the flow-induced rotation and deformation of the nucleus, and  $\Delta\Theta_2$  represents the contribution from local “ordered” structure due to the viscous flow. Note that  $\Delta\Theta_1$  and  $\Delta\Theta_2$  are functions of  $m_c$ , implying that Eq. (18) is an implicit expression of the critical nucleus number.

According to Eqs. (18)-(21), it is evident that the critical nucleus size is dependent on the average velocity of the Poiseuille flow and the spatial position of the nucleus in the circular channel. It is interesting to note that the critical nucleus size is also dependent on the atomic mass of the solute atoms and the number of solute atoms in the RVE.

For the stationary state, Eq. (15) yields

$$m_c^{-1/3} = -\frac{3}{8\pi\sigma} \left( \frac{3\Omega_2}{4\pi} \right)^{-2/3} \Delta\Theta \quad (22)$$

which is the same as the result of the classical nucleation theory. Note that Eq. (22) is derived from Eq. (15) under the condition that the term from the configurational entropy is set to be zero. There exists a discontinuity of the change of the Gibbs free energy between the stationary state and the flow state.

#### 4. Discussion

##### Formation of a liquid microcluster

For the formation of a liquid microcluster in a flow system, there is  $E_{SC} = 0$ . Let  $\Delta_m G (= N_a \Delta G / N_1)$  be the change of the Gibbs free energy per mole of the solvent for the system in the RVE from the flow state without a microcluster to the flow state with a microcluster. We have

$$\begin{aligned} \Delta_m G = & \frac{4\pi N_a m_2 \alpha^2 V^2}{15 N_1 \Omega_2} \left( \frac{r}{r_0^2} \right)^2 a^5 + [\mu_m - \mu_0 - kT \ln(\gamma_2 y)] \frac{4\pi N_a a^3}{3 N_1 \Omega_2} + 4\pi \sigma a^2 \frac{N_a}{N_1} \quad (23) \\ & + RT \left[ \ln \frac{1-y}{1-x} + \frac{N_2}{N_1} \ln \frac{y}{x} \right] \\ & - \frac{RT}{N_1} \left[ N_2 \ln \left( 1 - \frac{4\pi a^3}{3 N_2 \Omega_2} \right) - \frac{4\pi a^3}{3 \Omega_2} \ln \left[ 2 \left( N_2 - \frac{4\pi a^3}{3 \Omega_2} \right) m_2 V^2 \left( 1 - \frac{r^2}{r_0^2} \right)^2 \right] \right] \end{aligned}$$

Equation (23) represents the change of the Gibbs free energy per mole of the solvent for the local nucleation of a liquid microcluster in a finite system in a Poiseuille flow.

For  $N_1$  much larger than  $N_2$ , Eq. (23) is reduced to as

$$\Delta_m G = \frac{4\pi N_a m_2 \alpha^2 V^2}{15 N_1 \Omega_2} \left( \frac{r}{r_0^2} \right)^2 a^5 + \frac{4\pi N_a \Delta \Theta a^3}{3 N_1 \Omega_2} + 4\pi \sigma a^2 \frac{N_a}{N_1} \quad (24)$$

It is evident that the only contribution to the change of the Gibbs free energy is the kinetic energy from the rotational motion of the microcluster. At  $r = 0$ , i.e. the axisymmetric axis of the flow channel, Eq. (24) gives

$$\Delta_m G = \frac{4\pi N_a \Delta \Theta a^3}{3 N_1 \Omega_2} + 4\pi \sigma a^2 \frac{N_a}{N_1} \quad (25)$$

which is the same as the result of the classical nucleation theory. Such a result is in accord with that the spherical microcluster at the axisymmetric axis of the flow channel does not experience rotational motion.

Using Eq. (24) and taking the derivative with respect to  $a$ , we obtain the following equation

$$\frac{m_2 \alpha^2 V^2}{3\Omega_2} \left( \frac{r}{r_0^2} \right)^2 a^3 + \frac{\Delta\Theta}{\Omega_2} a + 2\sigma = 0 \quad (26)$$

in which the first and second terms represent the contributions of the kinetic energy due to the rotation of the microcluster and the change of chemical energy due to the phase change, respectively. The solutions of Eq. (26) for  $r \neq 0$  are

$$a_k = 2\sqrt{-\frac{p}{3}} \cos\left(\frac{1}{3} \arccos\left(\frac{3q}{2p} \sqrt{-\frac{3}{p}}\right) - \frac{2k\pi}{3}\right) \quad k = 0, 1, 2 \quad (27)$$

with

$$p = \frac{3\Delta\Theta}{m_2 \alpha^2 V^2} \left( \frac{r}{r_0^2} \right)^{-2} \quad \text{and} \quad q = \frac{6\sigma\Omega_2}{m_2 \alpha^2 V^2} \left( \frac{r}{r_0^2} \right)^{-2} \quad (28)$$

The critical nucleus size,  $a_c$ , is the smallest, positive root of Eq. (27). For  $r = 0$ , the critical nucleus size,  $a_c$ , for the nucleation of a critical nucleus at the axisymmetric axis is

$$a_c = -\frac{2\sigma\Omega_2}{\Delta\Theta} \quad (29)$$

### Formation of a solid microcluster

To analyze the formation of a solid microcluster, we focus on the homogeneous nucleation of a sucrose microcluster in an aqueous solution, which flows through a circular channel. Define  $\lambda$  as the ratio of the contribution of the kinetic energy from the rotation of the microcluster to the homogeneous nucleation of a sucrose crystal to the contribution of the change of chemical energy from the phase change to the homogeneous nucleation of a sucrose crystal in a viscous flow through a circular microchannel. From Eqs. (19) and (20), we have

$$\lambda = \frac{m_2 \alpha^2 V^2}{3\Delta\Theta} \left( \frac{r}{r_0^2} \right)^2 a^2 \quad (30)$$

Here,  $\alpha$  is  $\sim 1.5$ , as estimated from the results given by Jeong and Jang<sup>29</sup>.

The solubility of sucrose in water at 25 °C is 207 g in 100 g of water (67.47 g in 100 g solution)<sup>31</sup>, and the molecular weight of sucrose is 342.3 g/mol<sup>31</sup>. Using the result given by Saska and Myerson<sup>32</sup>, the specific interface energy between a sucrose microcluster and a sucrose-saturated aqueous solution is approximated to be 782.97 mJ/m<sup>2</sup>. The enthalpy of solution for the dissolution of sucrose in water is 16.7 kJ/mol<sup>33</sup>, which gives  $\Delta\Theta \approx -16.7$  kJ/mol. Using the molecular weight (342.3 g/mol) and density (1.587 g/cm<sup>3</sup>) of sucrose<sup>31</sup>, the molar volume of sucrose is found as

215.69 cm<sup>3</sup>/mol. Assume that the radius of the circular microchannel is 0.8 mm<sup>5</sup>, and the average velocity of the flow in the circular microchannel is 2.76 mm/s<sup>5</sup>.

Figure 2 shows the variation of the ratio,  $\lambda$ , at  $r = r_0$  with the size of a sucrose microcluster in the microchannel. It is evident that increasing the microcluster size increases the ratio, suggesting the increase of the contribution of the kinetic energy due to the rotation of the microcluster to the critical nucleus size of the glucose microcluster. However, the magnitude of the ratio,  $\lambda$ , is less than  $2 \times 10^{-16}$  for the microcluster size being up to 1  $\mu\text{m}$ , indicating that the effect of the kinetic energy due to the rotation of the microcluster on the critical nucleus size is negligible. Since the ratio,  $\lambda$ , is independent of the size of the system, as can be found from Eq. (30), the contribution of the kinetic energy due to the rotation of the microcluster to the nucleation of a sucrose microcluster in a finite system is negligible.

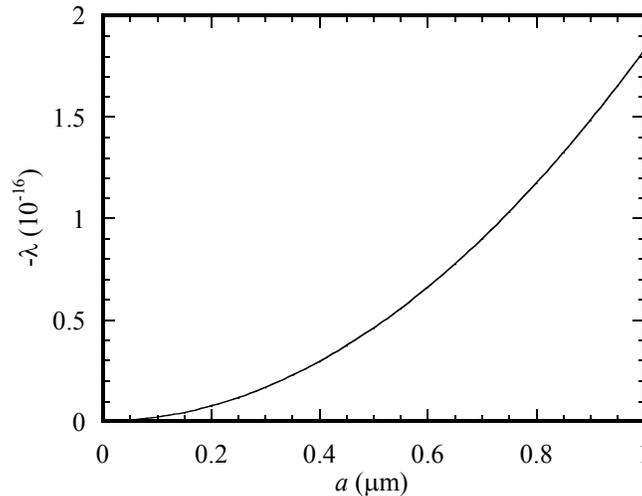


Figure 2. Variation of the ratio,  $\lambda$ , at  $r = r_0$  with the size of a glucose microcluster in a microchannel under a Poiseuille-flow.

The elastic modulus of crystalline sucrose is 32.3 GPa<sup>34</sup>. Assuming that the Poisson ratio of crystalline sucrose is 0.3, we obtain  $G=12.42$  GPa. The viscosity of a saturated, aqueous sucrose solution is 76.9 MPa·s<sup>31</sup>. Using Eqs. (19) and (20), we can calculate the ratio of the contribution of the flow-induced strain energy in the microcluster to the homogeneous nucleation of a sucrose crystal to the contribution of the change of chemical energy from the phase change to the homogeneous nucleation of a sucrose crystal in a viscous flow through a circular microchannel. Using the above data, the ratio is found to be  $-3.12 \times 10^{-26}$ . Such a small ratio suggests that the contribution of the flow-induced strain energy in the microcluster to the change of the Gibbs free

energy is negligible in comparison to the contribution from the change of chemical energy due to the phase change.

From the above analysis, we can conclude that the contributions of the kinetic energy and the flow-induced strain energy are negligible in the analysis of the homogeneous nucleation of sucrose crystals in the Poiseuille flow in a circular microchannel. It needs to be pointed out that such a conclusion is applicable to the homogeneous nucleation of most crystalline materials in microchannels, since they possess large moduli and the viscosities of the corresponding aqueous solutions are generally less than the viscosity of a saturated, aqueous sucrose solution. Thus, the change of the Gibbs free energy per mole of the solvent for the system in the RVE from the flow state without a microcluster to the flow state with a microcluster can be approximately expressed as

$$\Delta_m G = [\mu_m - \mu_0 - kT \ln(\gamma_2 y)] \frac{4\pi N_a a^3}{3N_1 \Omega_2} + 4\pi \sigma a^2 \frac{N_a}{N_1} + RT \left[ \ln \frac{1-y}{1-x} + \frac{N_2}{N_1} \ln \frac{y}{x} \right] \quad (31)$$

$$- \frac{RT}{N_1} \left( N_2 \ln \left( 1 - \frac{4\pi a^3}{3N_2 \Omega_2} \right) - \frac{4\pi a^3}{3\Omega_2} \ln \left[ 2 \left( N_2 - \frac{4\pi a^3}{3\Omega_2} \right) m_2 V^2 \left( 1 - \frac{r^2}{r_0^2} \right)^2 \right] \right)$$

Note that the ratio of  $N_2/N_1$  is associated with the concentration of the solute atoms ( $= N_2/(N_1 + N_2)$ ). To have nucleation and growth of a new phase, a supersaturated solution is needed, i.e.  $N_2/N_1$  being larger than the critical ratio of  $(N_2/N_1)_c$  corresponding to the solubility of the new phase in the solvent at given conditions (temperature and pressure).

## 5. Numerical illustration

Consider the homogeneous nucleation of a sucrose microcluster in an aqueous solution, which flows through a circular microchannel of 0.8 mm in radius. Assume that the size of an RVE for the formation of a sucrose microcluster in the microchannel is  $1 \times 1 \times 1 \mu\text{m}^3$  and the degree of local supersaturation is 2 times of the solubility of sucrose in water at 25 °C (207 g in 100 g of water). We have  $(N_1, N_2) = (14.519, 3.158)_2^{310^9}$ . Figure 3 presents the variation of the change of the Gibbs free energy per mole of the solvent for local nucleation of a sucrose microcluster with the microcluster size for the same values of  $N_1$  and  $N_2$  and the average flow speed of 2.76 mm/s. Similar to the classic nucleation theory, increasing the microcluster size causes the change of the Gibbs free energy to increase first, reach maximum, and then decrease for large microcluster size. The microcluster size corresponding to the largest change of the Gibbs free energy, which is

referred to as the work of formation of a critical nucleus ( $\Delta G_{\max}$ ), is the critical nucleus size. There exists spatial dependence of the change of the Gibbs free energy, which is associated with the spatial distribution of the flow field. The larger the distance to the axisymmetric axis, the smaller is the work of formation of a critical nucleus.

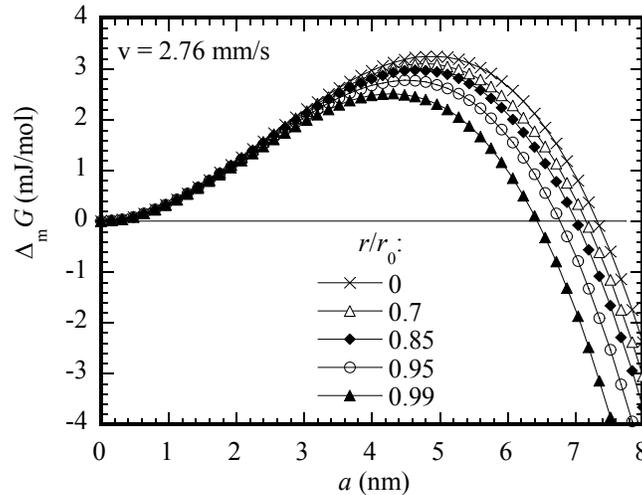


Figure 3. Dependence of the change of the Gibbs free energy on the microcluster size at different spatial positions in the radial direction for the same values of  $N_1$  and  $N_2$  ( $r_0$ : 0.8 mm,  $V$ : 2.76 mm/s).

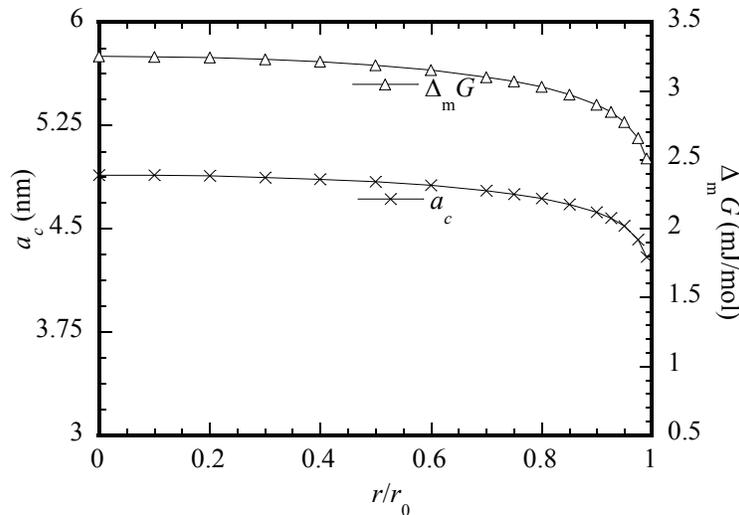


Figure 4. Dependence of the critical nucleus size and the corresponding work of formation of a critical nucleus on the spatial position in the radial direction for the Poiseuille flow in a circular microchannel for the same values of  $N_1$  and  $N_2$  ( $r_0$ : 0.8 mm,  $V$ : 2.76 mm/s)

Using the results in Fig. 3, we can calculate the work of formation of a critical nucleus and the corresponding critical nucleus size for the homogeneous nucleation of a sucrose nucleus at

different spatial positions in the radial direction. Figure 4 shows the dependence of the work of formation of a critical nucleus and the corresponding critical nucleus size on the spatial position in the radial direction for the same values of  $N_1$  and  $N_2$ . Both the critical nucleus size and the corresponding work of formation of a critical nucleus decrease with the increase of the distance to the axisymmetric axis, revealing the dependence of the critical nucleus size on local flow field. The smaller the distance to the axisymmetric axis, the larger is the critical nucleus size. The relative difference of the critical nucleus size is 12.1%.

Mokshin et al.<sup>14</sup> revealed the increase of the effective temperature with the increase of shear rate in the MD simulation of the nucleation of a single-component glass-forming system under a uniform shear rate. It is known that the nucleation behavior can be expressed by the Arrhenius relation with the energy barrier being the work of formation of a critical nucleus. The increase of the effective temperature with the increase of shear rate from the work given by Mokshin et al.<sup>14</sup> suggests that increasing shear rate reduces the work of formation of a critical nucleus. Liu and Rasmuson<sup>20</sup> observed the decrease of the induction time for the nucleation of butyle paraben in ethanol with the increase of shear rate in a Taylor-Couette flow system. They assumed that the induction time is inversely proportional to the nucleation rate and observed the linear correlation between the logarithm of the induction time and the temperature term. Such a correlation reveals that increasing shear rate resulted in the decrease of the energy barrier for the nucleation of butyle paraben.

For the Poiseuille flow of  $V_L = 2V[1-(r/r_0)^2]$  in a circular microchannel, local shear rate is  $4Vr/r_0^2$  and increases with the increase of the distance to the axisymmetric axis. The results shown in Fig. 4 indicates that increasing the shear rate leads to the decrease of the work of formation of a critical nucleus. Such a trend is in consistence with that reported by Mokshin et al.<sup>14</sup> and Liu and Rasmuson<sup>20</sup>. It needs to be pointed out that there exists spatial distribution of the solute concentration, as revealed by Taylor<sup>23</sup>, in the radial direction of the circular microchannel. Such a spatial distribution of the solute concentration reduces the extent of oversaturation, likely leading to the changes in local critical nucleus size and the corresponding work of formation of a critical nucleus due to the dependence of the change of the Gibbs free energy on local concentration of solute atoms/particles.

From Figs. 3 and 4, we note that the critical nucleus size decreases with the increase of the distance to the axisymmetric axis, i.e. the critical nucleus size decreases with the increase of the

shear rate. This trend is in contrast to the result obtained by Blaak et al.<sup>21</sup> that the critical size increases with increasing the shear rate. Such different behavior is likely due to that Blaak et al.<sup>21</sup> assumed linear dependences of the chemical potential difference and interfacial energy on the square of shear rate in their analysis, leading to the increase of the change of the Gibbs free energy with the increase of shear rate, as shown in Fig. 2 in their work. However, Blaak et al.<sup>21</sup> stated “this observation should not be considered as evidence that the shear rate can really be considered as a thermodynamic variable”. Thus, it remains elusive whether one can include the contribution of shear rate to the interfacial energy.

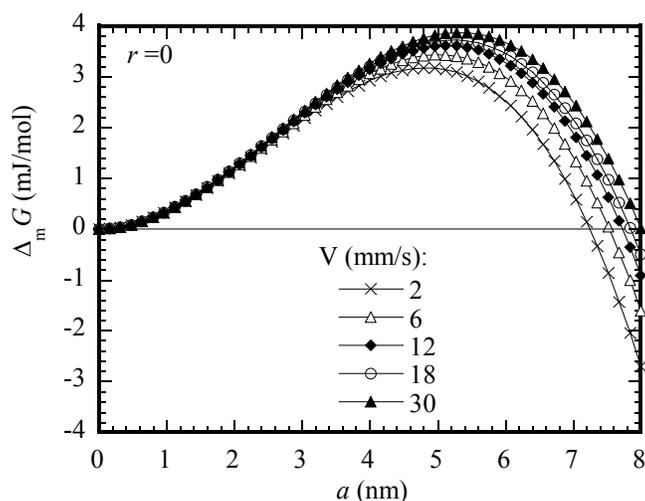


Figure 5. Variation of the change of the Gibbs free energy with the microcluster size at axisymmetric axis for the same values of  $N_1$  and  $N_2$  under different average flow speeds ( $r_0$ : 0.8 mm).

Figure 5 depicts the variation of the change of the Gibbs free energy with the microcluster size at axisymmetric axis for the same values of  $N_1$  and  $N_2$  under different average flow speeds. It is evident that there exists the dependence of the change of the Gibbs free energy on the average flow speed of the Poiseuille flow in a circular microchannel. The variation of the change of the Gibbs free energy with the microcluster size is similar to the classical nucleation theory, independent of the magnitude of average flow speed.

Using the results in Fig. 5, we calculate the work of formation of a critical nucleus and the corresponding critical nucleus size for the homogeneous nucleation of a sucrose nucleus at the axisymmetric axis for different average flow speeds. Figure 6 presents the dependence of the work of formation of a critical nucleus and the corresponding critical nucleus size on the average flow

speed at the axisymmetric axis for the same values of  $N_1$  and  $N_2$ . Both the critical nucleus size and the corresponding work of formation of a critical nucleus increase with the increase of the average flow speed, revealing the effect of the flow speed of the critical nucleus size and the corresponding work of formation of a critical nucleus. The larger the flow speed, the larger are the critical nucleus size and the corresponding work of formation of a critical nucleus. It needs to be pointed out that there is no effect of the shear rate, since the shear rate is zero at the axisymmetric axis.

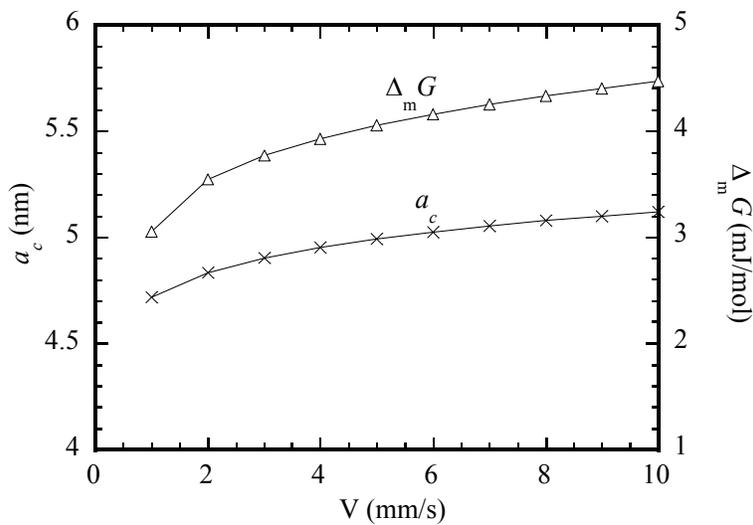


Figure 6. Variation of the critical nucleus size and the corresponding work of formation of a critical nucleus with average flow speed at axisymmetric axis for the same values of  $N_1$  and  $N_2$  ( $r_0$ : 0.8 mm).

## 6. Discussion

The above analysis has been focused on a single microcluster in spherical shape. In general, multi-microclusters of nonspherical shapes, such as cube and cylinder, can be present. The above analysis can be extended to study the nucleation of new phases of nonspherical shapes and polynucleation.

For isotropic interfacial energy, both the surface area and volume of a nonspherical microcluster need to be calculated; for anisotropic interfacial energy, integration over the surface of the nonspherical microcluster is needed in the calculation of the interfacial energy. The numbers of the solute atoms on the surface of the microcluster and those enclosed by the microcluster can be calculated from the surface area and volume of the nonspherical microcluster. Following the same approach, we can find the change of the Gibbs free energy in a flow field and determine the critical number of solute atoms for the nucleation of a critical nucleus of nonspherical shape.

There are two approaches to analyze polynuclear scenario. One is based on simultaneous nucleation, and the other is based on the kinetic approach developed by Zeldovich<sup>35</sup>. For the simultaneous nucleation, there is only a limited number of solvent and solute atoms confined in a finite space (domain) for the formation of a nucleus. Introducing the domain size and fixed numbers of the solvent and solute atoms in the corresponding domain and following similar approach presented in previous section, the effect of the domain size on the change of the Gibbs free energy can be formulated and the dependence of the critical nucleus size on the domain size can be determined. We can also use the kinetic approach developed by Zeldovich<sup>35</sup> to determine if “simultaneous” nucleation can occur. In this approach, the nucleation barrier (the work of formation of a critical nucleus) as derived in the above analysis can be used in the calculation of the nucleation rate and in the determination of the critical nucleation rate. Using the critical nucleation rate and the critical nucleus size, we can determine the time interval for the occurring of two consecutive nucleation events and the presence of mono-nucleation or poly-nucleation.

## 7. Conclusion

The success in the synthesis of objects of nanosizes in dynamic environments has stimulated great interest in understanding the effects of fluid flow on the nucleation processes under fluid flow and agitation. Using the result given by Barsky<sup>25</sup>, we have determined the configuration entropy associated with the kinetic energies of the solvent and solute atoms and incorporated the configuration entropy as well as the kinetic energy and strain energy of a microcluster in the calculation of the change of the Gibbs free energy of a REV between a flow state without the microcluster and the corresponding flow state with the microcluster for the Poiseuille flow in a circular microchannel. The change of the Gibbs free energy is a function of the average flow speed and the spatial position in the radial direction.

Following the approach used in the classic nucleation theory, we have derived the analytical expression for the determination of the critical nucleus size. For the formation of a critical liquid nucleus, the liquid nucleus cannot sustain shear deformation, and the contribution from the strain energy to the change of the Gibbs free energy is null. We have obtained analytical solution of the critical nucleus size. For the formation of a critical solid nucleus, the contributions from both the kinetic energy and the strain energy are generally negligible in comparison to the chemical energy associated with the phase change from individual monomers/particles in a solution to a solid nucleus. The configuration entropy associated the kinetic energies of the solvent and solute atoms

determines the difference of the change of the Gibbs free energy between a stationary state and a flow state for the formation of a solid nucleus.

The numerical results for the homogeneous nucleation of a sucrose microcluster in a REV of an aqueous solution, which flows through a circular microchannel, shows that both the critical nucleus size and the corresponding work of formation of a critical nucleus decrease with the increase of the distance to the axisymmetric axis for the same values of  $N_1$  and  $N_2$ . Increasing average flow speed leads to the increases in the critical nucleus size and the corresponding work of formation of a critical nucleus at the same spatial position under the same values of  $N_1$  and  $N_2$ .

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