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Nucleation in a liquid droplet

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The droplet-based microreactors in microfluidic systems have been used to synthesize nanocrystals of a variety of metals and semiconductors, which involves the nucleation and growth processes. Considering the limited numbers of solvent atoms and solute atoms/particles in a stationary droplet, we derive analytical expressions of the changes of the Gibbs free energy and the Helmholtz free energy for the concurrent formation of multiple microclusters of the same size in the liquid droplet. Both the changes of the Gibbs free energy and the Helmholtz free energy are dependent on the ratio of the number of microclusters to the solvent atoms and the interface energy between the solution and the microclusters. Using the change of the free energy, which is an approximation of the Gibbs free energy and the Helmholtz free energy, we obtain the critical nucleation number of the solute atoms/particles in the microclusters for the concurrent nucleation of multiple nuclei of the same size. The critical nucleation number of the solute atoms/particles is dependent on the ratio of the number of nuclei in the droplet to the solvent atoms, and the maximum change of the free energy for the concurrent nucleation of multiple nuclei of the same size increases with the increase of the ratio of the number of the nuclei in the droplet to the number of the solvent atoms.

Introduction

Nanoscale materials, such as quantum dots, nanowires and nanoplates, have attracted great interest due to their tunable electro-optical properties and a wide range of applications, including nanophotonics and microelectronics. The methods used to synthesize nanoscale materials can be grouped generally into two categories:[1] one is the top-down methods with the generation of nanoscale materials from the "breaking" of the corresponding bulk phases, and the other is the bottom-up methods with the generation of nanoscale materials from the assembly of monomers (atoms and molecules). Among the bottom-up methods, the microreactions in microfluidic systems[2–8] have provided a unique approach for the mass production of nanoscale materials. There are two basic modes for the microreactions in microfluidic systems: one involves the nucleation and growth of nanoscale materials in a continuous flow field,[3,8–10] and the other confines the nucleation and growth of nanoscale materials in droplets suspended in a continuous flow field.[3,11] The applications of nanoscale materials, especially semiconductor nanocrystals, are dependent on the size distribution and geometries of the materials. Controlling the nucleation of nanoscale materials in the microreactions in microfluidic systems is one of the key steps to produce nanoscale materials with the desired properties, size distribution (monodispersed nanocyrstals) and geometries. Thus, it is of great importance to understand the nucleation of nanoscale materials in the microreactions in microfluidic systems.

According to the theory of thermodynamics,[12] the driving force for the nucleation of new phases is the decrease of the free energy, such as the Gibbs free energy in the classical nucleation theory,[12–14] which has been successfully used in the study of the nucleation of a liquid/solid phase from the corresponding vapor/liquid phase of the same material. Realizing the local density fluctuations in liquid solutions, which limits the use of the classical nucleation theory, a two-step nucleation theory[13,15,16] has been developed. The two-step nucleation theory involves two energy barriers; one is the energy barrier needed to be overcome for the formation of dense precursors, and the other is the energy barrier for the nucleation of crystalline nuclei from the dense precursors. However, both theories are based on unlimited atoms/particles for the nucleation, *i.e.*, nucleation in an infinite system.

Considering the limited numbers of atoms/particles in a finite system, Vogelsberger[17] analyzed the nucleation of multiple liquid microclusters/droplets from the corresponding vapor phase and pointed out the need to use the Helmholtz free energy instead of the Gibbs free energy. Schmelzer and Ulbricht[18] used the Helmholtz free energy to analyze the depletion effect on the nucleation and growth for the first-order phase changes in a finite system of a single component. Modifying the classical nucleation theory, Grossier and Veesler[19] studied the dependence of the critical cluster size on the confinement in an infinite system.

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Currently, there are only a very few studies focusing on the nucleation of multiple microclusters from liquid solutions of finite systems, which plays an important role in understanding the synthesis of nanoscale materials from the droplet-based microreactors in microfluidic systems.

The purpose of this work is to study the concurrent nucleation of multiple microclusters of the same size in a stationary, spherical droplet of a liquid solution consisting only of the solvent atoms and the solute atoms/particles at a constant temperature. Both the Gibbs free energy and the Helmholtz free energy are derived as a function of the numbers of the solvent atoms and the solute atoms/particles. Considering nanocrystals of multiple topologies,[8] which are formed from the microreactions in microfluidic systems, we analyze the critical nucleation numbers/sizes for microclusters of three different topologies (sphere, cube and disk).

Theoretical model

We consider a stationary liquid droplet immersed in an immiscible liquid medium, as shown in Fig. 1, to mimic the nucleation of nanocrystals in the droplet-based microreactors in microfluidic systems. The liquid droplet of r_0 in radius consists only of solvent atoms and solute atoms/particles, and the numbers of the solvent atoms and solute atoms/particles are N_1 and N_2, respectively. There is no mass exchange between the liquid droplet and the immiscible liquid medium; the liquid droplet forms a closed system. The liquid droplet is initially in a supersaturated state (Fig. 1a), which leads to the concurrent nucleation of multiple microclusters at the nucleation state (Fig. 1b).

We define the atomic fraction of the solute atoms/particles, x, as

$$x = \frac{N_2}{N_1 + N_2}. \tag{1}$$

The chemical potential per solvent atom, μ_1, at the supersaturated state is

$$\mu_1 = \mu_1^0 + kT\ln[\gamma_1(1 - x)] \tag{2}$$

where μ_1^0 is the chemical potential of pure solvent atoms in the standard state, k is the Boltzmann constant, T is the absolute temperature, and γ_1 is the activity coefficient for the solvent atoms. The chemical potential per solute atom, μ_2, in the supersaturated state is

$$\mu_2 = \mu_2^0 + kT\ln(\gamma_2 x) \tag{3}$$

with μ_2^0 being the chemical potential of pure solute atoms in the standard state and γ_2 being the activity coefficient for the solute atoms. Using eqn (2) and (3), we obtain the Gibbs free energy of the liquid droplet in the supersaturated state, G_{init}, as

$$G_{\text{init}} = N_1\mu_1 + N_2\mu_2 + 4\pi {r_0}^2\sigma_{\text{i}}^{\text{s}} = N_1(\mu_1^0 + kT\ln[\gamma_1(1 - x)]) + N_2(\mu_2^0 + kT\ln(\gamma_2 x)) + 4\pi {r_0}^2\sigma_{\text{i}}^{\text{s}} \tag{4}$$

in which $\sigma_{\text{i}}^{\text{s}}$ is the specific interface tension between the liquid droplet in the supersaturated state and the immiscible liquid medium. In general, the specific interface tension of a droplet varies with the fraction of the solute atoms/particles. According to the semi-empirical relation given by Szyszkowski,[20,21] the specific interface tension, $\sigma_{\text{i}}^{\text{s}}$, is a function of the concentration of the solute atoms/particles in the liquid droplet as described by

$$\sigma_{\text{i}}^{\text{s}} = \sigma_{\text{pure}} - \Gamma kT\ln(1 + x/\gamma_1) \tag{5}$$

where σ_{pure} is the interface tension of the pure solvent, and Γ is the maximum surface excess.

Consider that there are n microclusters nucleated concurrently in the liquid droplet in the nucleation state. For simplicity, we assume that all the microclusters exhibit the same topology and have the same number of solute atoms, m. The nucleation of n microclusters leads to a decrease of the number of solute atoms/particles in the solvent to $N_2 - nm$. We define the atomic fraction of the solute atoms/particles dispersed in the solvent, y, in the nucleation state as

$$y = \frac{N_2 - nm}{N_1 + N_2 - nm} \tag{6}$$

The Gibbs free energy of the liquid droplet without the contribution from the microclusters and the interfaces between the microclusters and the solution in the liquid droplet, G_{l}, is

$$G_{\text{l}} = N_1(\mu_1^0 + kT\ln[\gamma_1(1 - y)]) + (N_2 - nm)(\mu_2^0 + kT\ln(\gamma_2 y)) + 4\pi {r_{\text{f}}}^2\sigma_{\text{f}}^{\text{s}} \tag{7}$$

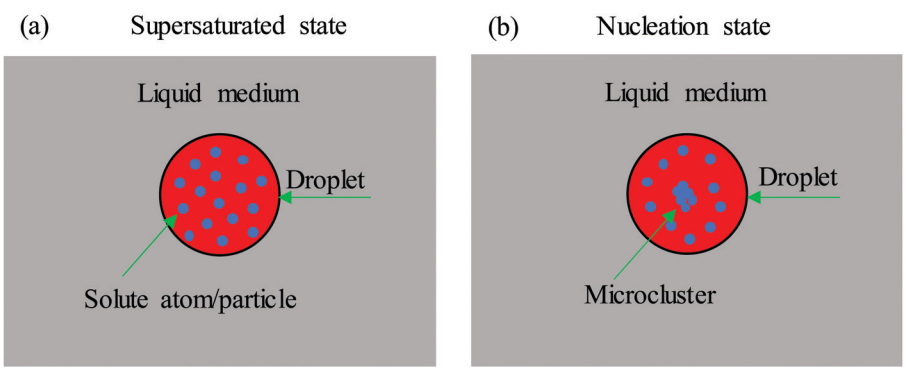

Fig. 1 Schematic of a liquid droplet suspended in an immiscible liquid medium: (a) supersaturated state, and (b) nucleation state with a microcluster.

where r_f is the radius of the liquid droplet in the nucleation state, and σ_f^s is the specific interface tension between the liquid droplet in the nucleation state and the immiscible liquid medium. The dependence of the specific interface tension, σ_f^s, on the concentration, y, can be expressed as eqn (5) with the replacement of x by y.

The Gibbs free energy associated with the nucleation of a single microcluster, G_c, is

$$G_c = \mu_m m + f(\sigma_m) \tag{8}$$

in which μ_m is the chemical potential per solute atom in the microcluster, and $f(\sigma_m)$ is the interface energy determined by the specific interfacial energy, σ_m, for the interface between the microcluster and the solution in the nucleation state and the surface area of the microcluster. Similar to the interface tension of the liquid droplet (eqn (5)), the specific interface energy, σ_m, is dependent generally on the concentration of the solute atoms/particles.[22] It is worth mentioning that the interfacial energy of the interface between a crystal and a liquid is a function of the solubility of the crystal in the liquid[22] and plays an important role in the nucleation of the microclusters.

From eqn (7) and (8), we obtain the Gibbs free energy of the liquid droplet with n microclusters as

$$\begin{aligned} G_{final} = {} & N_1(\mu_1^0 + kT\ln[\gamma_1(1-y)]) + (N_2 - nm)(\mu_2^0 + kT\ln(\gamma_2 y)) \\ & + 4\pi r_f^2\sigma_f^s + n[\mu_m m + f(\sigma_m)] \end{aligned} \tag{9}$$

Using eqn (4) and (9), the change of the Gibbs free energy due to the concurrent nucleation of n microclusters, ΔG, is found as

$$\begin{aligned} \Delta G &= G_{final} - G_{int} \\ &= N_1 kT\ln\frac{1-y}{1-x} + N_2 kT\ln\frac{y}{x} \\ &\quad - nm\left[\mu_2^0 + kT\ln(\gamma_2 y) - \mu_m\right] \\ &\quad + 4\pi\left(r_f^2\sigma_f^s - r_0^2\sigma_i^s\right) + nf(\sigma_m) \end{aligned} \tag{10}$$

In contrast to the classical nucleation theory, the change of the Gibbs free energy is dependent on the numbers of the solvent atoms and the solute atoms/particles in the supersaturated state and the interface tension for the interface between the liquid droplet and the immiscible liquid medium.

According to the Laplace relation, the pressure difference between the pressure, p_0, in the immiscible liquid medium and the pressure, p, inside a liquid droplet of r in radius as a function of the interface tension, σ, is

$$p - p_0 = \frac{2\sigma}{r} \tag{11}$$

That is to say, the constant pressure needed for the use of the Gibbs free energy is not satisfied. In general, the pressure or volume of the liquid droplet in the supersaturated state is likely different from the corresponding one of the liquid droplet in the nucleation state,[23] since the volume of a microcluster is not simply equal to the summation of the volumes of the corresponding atoms/particles in a liquid solution, and the pressure inside the liquid droplet is dependent on the concentration of the solute atoms and the droplet size.

It is known that the concentration of the solvent atoms is assumed to be constant and the system is infinite in the classical nucleation theory.[24] The driving force for the nucleation of the microclusters is solely determined by the concentration of the solute atoms with $(r_f^2\sigma_f^s - r_0^2\sigma_i^s) \to 0$ and $y/x \to 1$, and there is no interaction between the microclusters. One can focus on the nucleation of only one microcluster, *i.e.*, $n = 1$, and simplify eqn (10) as

$$\Delta G = m\Delta G_m + f(\sigma_m) \text{ and } \Delta G_m = \mu_m - [\mu_2^0 + kT\ln(\gamma_2 x)] \tag{12}$$

Eqn (12) is the same as the result in the classical nucleation theory.[24,25]

According to the theory of thermodynamics,[26] the Helmholtz free energy, F, can be calculated from the Gibbs free energy as

$$F = G - \tilde{p}V \tag{13}$$

in which $\tilde{p}$ is the pressure of the system at equilibrium state, and V is the volume of the system. From eqn (10) and (13), we obtain the change of the Helmholtz free energy of the liquid droplet from the supersaturated state to the nucleation state as

$$\begin{aligned} \Delta F &= N_1 kT\ln\frac{1-y}{1-x} + N_2 kT\ln\frac{y}{x} - nm\left[\mu_2^0 + kT\ln(\gamma_2 y) - \mu_m\right] \\ &\quad + 4\pi r_0^2\left(\sigma_f^s - \sigma_i^s\right) + nf(\sigma_m) + n(p_f - p_m)V_m + (p_i - p_f)V_0 \end{aligned} \tag{14}$$

where p_i, p_f and p_m are the pressures in the liquid droplet in the supersaturated state, in the liquid droplet in the nucleation state and in the microclusters, respectively, and V_0 and V_m are the volumes of the liquid droplet and an individual microcluster, respectively.

Using eqn (5) and (11), the pressure difference of $(p_i - p_f)$ is found to be

$$p_i - p_f = \frac{2\left(\sigma_i^s - \sigma_f^s\right)}{r_0} = \frac{2\Gamma kT}{r_0}\ln\frac{\gamma_1 + x}{\gamma_1 + y} \tag{15}$$

Substituting eqn (15) in eqn (14) yields

$$\begin{aligned} \Delta F &= N_1 kT\ln\frac{1-y}{1-x} + N_2 kT\ln\frac{y}{x} - nm\left[\mu_2^0 + kT\ln(\gamma_2 y) - \mu_m\right] \\ &\quad + n(p_f - p_m)V_m + nf(\sigma_m) - \frac{4\Gamma\pi r_0^2 kT}{3}\ln\frac{\gamma_1 + x}{\gamma_1 + y} \end{aligned} \tag{16}$$

Similar to the change of the Gibbs free energy, the change of the Helmholtz free energy is dependent on the numbers of the solvent atoms and the solute atoms/particles in the supersaturated state as well as the interface energy for the interface between the liquid droplet and the microclusters. Note that the pressure difference of $(p_f - p_m)$ is dependent on the interface energy for the interface between the liquid droplet and the microclusters and the size and topology of the microclusters.

It is known that both the liquid and solid phases can be approximated as incompressible in comparison to the

corresponding gas phase.[26] Thus, we can assume that the volume difference between a microcluster and the summation of the volumes of the corresponding atoms in the aqueous solution are negligible. Such an approach is similar to that used by Philippe,[27] who assumed the same particle sizes (atomic volumes) for both phases. Note that Philippe[27] did not provide explicit expressions of chemical potentials and limited the study to the nucleation of one single cluster. Thus, the volume of the liquid droplet in the nucleation state is approximately the same as in the supersaturated state, *i.e.*, $r_f = r_0$. Under such a condition, it is likely more appropriate to use the Helmholtz free energy than the Gibbs energy to analyze the nucleation in a finite system.[17]

As pointed out above, the pressure and volume of the liquid droplet in the supersaturated state are likely different from the corresponding ones of the liquid droplet in the nucleation state due to the difference in the average distance between particles/atoms in the two phases, which is dependent on the interaction between particles/atoms. There are a few parameters in eqn (16), such as γ_i (i = 1, 2) and Γ, which require experimental studies, including the measurement of contact angles, to determine the variation of the parameters at a given temperature with the concentration of the solute atoms/particles in the solvent for the numerical calculation. Considering that the pressure change in the liquid droplet or the volume change of the liquid droplet is approximately negligible during the nucleation of the microclusters and the sizes of the microclusters are on the nanoscale, we approximate the change of the free energy of the droplet as

$$\Delta\Psi = N_1 kT \ln\frac{1-y}{1-x} + N_2 kT \ln\frac{y}{x} - nm\Delta\Theta + nf(\sigma_m) \quad (17)$$

with $-\Delta\Theta = \mu_m - [\mu_2^0 + kT\ln(\gamma_2 y)]$, which represents the change of the chemical potential for the transition of a solute atom/particle in the liquid droplet to the microclusters. Note that σ_m in eqn (17) is approximated as a constant. Correspondingly, eqn (17) can be treated as the first order approximation of both eqn (10) and (16). Using eqn (17), we obtain the change of the free energy per mole of the solvent, $\Delta_m\Psi$, as

$$\begin{aligned}\Delta_m\Psi &= \frac{N_a\cdot\Delta\Psi}{N_1}\\ &= RT\ln\frac{1-y}{1-x} + \frac{N_2}{N_1}RT\ln\frac{y}{x} - \frac{nm}{N_1}\Delta_m\Theta\\ &\quad + \frac{n}{N_1}N_a f(\sigma_m)\end{aligned} \quad (18)$$

where N_a is the Avogadro constant, R is the gas constant, $-\Delta_m\Theta$ is the change of the chemical potential for the transition of one mole of the solute atoms/particles in the liquid droplet to the microclusters. Substituting eqn (1) and (6) in eqn (18) yields

$$\begin{aligned}\Delta_m\Psi &= -RT\ln\left(1-(1-x)\frac{nm}{N_1}\right)\\ &\quad + \frac{x}{1-x}RT\ln\left(\frac{1}{x}\cdot\frac{x-(1-x)nm/N_1}{1-(1-x)nm/N_1}\right)\\ &\quad - \frac{nm}{N_1}\Delta_m\Theta + \frac{nN_a}{N_1}f(\sigma_m)\end{aligned} \quad (19)$$

Here, $f(\sigma_m)$ is a function of m and the geometrical shape of the microclusters. It is evident that the change of the free energy is a function of the ratio of n/N_1.

Critical nucleation number in a microcluster for homogeneous nucleation

According to the nucleation theory, the critical nucleation size for homogenous nucleation in the liquid droplet can be determined from the change of the free energy per mole of the solvent, $\Delta_m\Psi$, as

$$\left.\frac{\partial\Delta_m\Psi}{\partial V_m}\right|_{T,V_0,N_1,N_2,n} = \left.\frac{\partial\Delta_m\Psi}{\partial m}\right|_{T,V_0,N_1,N_2,n} = 0 \quad (20)$$

Note that the critical nucleation size is a monotonic function of the critical nucleation volume (the critical number of solute atoms/particles) in the nucleus. Substituting eqn (19) in eqn (20), we have

$$\begin{aligned}\frac{df(\sigma_m)}{dm} &= \Delta\Theta\\ &\quad + \frac{kT(1-x)^2}{[1-(1-x)nm/N_1][x-(1-x)nm/N_1]}\frac{nm}{N_1}\end{aligned} \quad (21)$$

For $N_1 \to \infty$, eqn (21) becomes

$$\frac{df(\sigma_m)}{dm} = \Delta\Theta \quad (22)$$

which is the same as the result in the classical nucleation theory. According to eqn (21), we can conclude that the critical nucleation size for the homogenous nucleation in the liquid droplet is dependent on the degree of saturation in the liquid droplet and the ratio of the number of the microclusters/nuclei to the total number of the solvent atoms.

In the following, we consider three different geometrical shapes (sphere, cube and disk) under the condition that the local change of the concentration of the solute atoms/particles has a negligible effect on the interface energy for the interface between the solution and the microclusters due to the small change of the concentration of the solute atoms/particles near the interface.

For a spherical nucleus/microcluster of r in radius, the surface area and volume are $4\pi r^2$ and $4\pi r^3/3$, respectively. Therefore,

$$m = \frac{4\pi N_a r^3}{3\Omega} \text{ and } f(\sigma_m) = 4\pi r^2\sigma_m = 4\pi\sigma_m\left(\frac{3m\Omega}{4\pi N_a}\right)^{2/3} \quad (23)$$

with Ω being the molar volume of the solute atoms/particles. Substituting eqn (23) in eqn (21) yields

$$\begin{aligned}m_c^{-1/3} &= \frac{3}{8\pi\sigma_m}\left(\frac{3\Omega}{4\pi N_a}\right)^{-2/3}\\ &\quad\times\left(\Delta\Theta + \frac{kT(1-x)^2}{[1-(1-x)nm_c/N_1][x-(1-x)nm_c/N_1]}\frac{nm_c}{N_1}\right)\end{aligned} \quad (24)$$

which gives the critical nucleation number of the solute atoms/particles, m_c, for the critical nucleation size of the spherical

nuclei in the liquid droplet. Here, the subscript "c" represents "critical". Eqn (24) reveals that the critical nucleation number of the solute atoms/particles is a function of the degree of saturation, the total number of solvent atoms and the number of microclusters/nuclei in the liquid droplet. For $N_1 \rightarrow \infty$, eqn (24) gives

$$m_c = \left(\frac{8\pi\sigma_m}{3\Delta\Theta}\right)^3 \left(\frac{3\Omega}{4\pi N_a}\right)^2 \quad \text{and} \quad r_c = \frac{2\Omega\sigma_m}{N_a\Delta\Theta} \tag{25}$$

in which r_c is the critical nucleation size of the spherical nuclei. It is evident that the critical nucleation size, r_c, is the same as that in the classical nucleation theory.

For a cubic nucleus/microcluster of a in length, the surface area and volume are $6a^2$ and a^3, respectively. Therefore, we have

$$m = \frac{N_a a^3}{\Omega} \quad \text{and} \quad f(\sigma_m) = 6a^2\sigma_m = 6\sigma_m\left(\frac{m\Omega}{N_a}\right)^{2/3} \tag{26}$$

Substituting eqn (26) in eqn (21) yields

$$m_c^{-1/3} = \frac{1}{4\sigma_m}\left(\frac{\Omega}{N_a}\right)^{-2/3} \times \left(\Delta\Theta + \frac{kT(1-x)^2}{[1-(1-x)nm_c/N_1][x-(1-x)nm_c/N_1]}\frac{nm_c}{N_1}\right) \tag{27}$$

which gives the critical nucleation number of the solute atoms/particles, m_c, for the critical nucleation size of the cubic nuclei in the liquid droplet. Similar to the nucleation of spherical microclusters, the critical nucleation number of the solute atoms/particles is a function of the degree of saturation, the total number of solvent atoms and the number of microclusters/nuclei in the liquid droplet. For $N_1 \rightarrow \infty$, eqn (27) gives

$$m_c^{-1/3} = \frac{\Delta\Theta}{4\sigma_m}\left(\frac{\Omega}{N_a}\right)^{-2/3} \quad \text{and} \quad a_c = \frac{4\sigma_m\Omega}{N_a\Delta\Theta} \tag{28}$$

For a disk-like nucleus/microcluster of h in thickness and r in radius, the volume is $\pi r^2 h$. There are three surfaces: top and bottom surfaces and side surface. The areas of the top and bottom surfaces are πr^2, and the area of the side surface is $2\pi rh$. The interface energy, $f(\sigma_m)$, is

$$f(\sigma_m) = 2\pi r^2\sigma_1 + 2\pi rh\sigma_2 \tag{29}$$

with σ_1 and σ_2 being the specific interface energies of the top/bottom surface and the side surface, respectively. Under the condition of a constant volume, the ratio of h/r, at which the interface energy, $f(\sigma_m)$, is minimum, is

$$\frac{r}{h} = \frac{\sigma_1}{2\sigma_2} \tag{30}$$

The number of solute atoms/particles in the disk-like nucleus/microcluster and the function, $f(\sigma_m)$, are then found to be

$$m = \frac{\pi r^2 hN_a}{\Omega} = \frac{2\pi r^3\sigma_2 N_a}{\sigma_1\Omega} \quad \text{and} \quad f(\sigma_m) = 2\pi\sigma_1\left(\frac{\sigma_1\Omega m}{2\pi\sigma_2 N_a}\right)^{2/3}\left(1+\frac{2\sigma_2^2}{\sigma_1^2}\right) \tag{31}$$

Substituting eqn (31) in eqn (21) yields

$$m_c^{-1/3} = \frac{3}{4\pi\sigma_1}\left(\frac{\sigma_1\Omega}{2\pi\sigma_2 N_a}\right)^{-2/3}\left(1+\frac{2\sigma_2^2}{\sigma_1^2}\right)^{-1} \times \left(\Delta\Theta + \frac{kT(1-x)^2}{[1-(1-x)nm_c/N_1][x-(1-x)nm_c/N_1]}\frac{nm_c}{N_1}\right) \tag{32}$$

which gives the critical nucleation number of the solute atoms/particles for the critical nucleation size of the disk-like nuclei in the liquid droplet. Similar to the nucleation of spherical microclusters, the critical nucleation number of solute atoms/particles is a function of the degree of saturation, the total number of solvent atoms and the number of microclusters/nuclei in the liquid droplet. For $N_1 \rightarrow \infty$, eqn (32) gives

$$m_c^{-1/3} = \frac{3\Delta\Theta}{4\pi\sigma_1}\left(\frac{\sigma_1\Omega}{2\pi\sigma_2 N_a}\right)^{-2/3}\left(1+\frac{2\sigma_2^2}{\sigma_1^2}\right)^{-1} \text{ and } r_c = \frac{2\sigma_1^2\Omega}{3\sigma_2 N_a\Delta\Theta}\left(1+\frac{2\sigma_2^2}{\sigma_1^2}\right) \tag{33}$$

According to eqn (24), (27) and (32), we note that the effect of the finite system on the critical nucleation number of the solute atoms/particles (critical nucleation size) is represented by the term of nm_c/N_1. Decreasing the number of solvent atoms increases the relative fraction of the contribution of the associated term in comparison with the term of $\Delta\Theta$, suggesting that the smaller the liquid droplet, the stronger the effect of the number of solvent atoms on the critical nucleation number of the solute atoms/particles (the critical nucleation size).

We define an auxiliary parameter, χ, as

$$\chi = 1 + \frac{kT(1-x)^2}{[1-(1-x)nm_c/N_1][x-(1-x)nm_c/N_1]}\frac{nm_c}{N_1\Delta\Theta} \tag{34}$$

From eqn (24), (27) and (32), we have

$$\frac{m_c^{-1/3}}{\chi} = \frac{\Delta\Theta}{4}\left(\frac{\Omega}{N_a}\right)^{-2/3} \times \begin{cases} \dfrac{3}{2\pi\sigma_m}\left(\dfrac{3}{4\pi}\right)^{-2/3} & \text{spherical microclusters} \\ \dfrac{1}{\sigma_m} & \text{for cubic microclusters} \\ \dfrac{3}{\pi\sigma_1}\left(\dfrac{\sigma_1}{2\pi\sigma_2}\right)^{-2/3}\left(1+\dfrac{2\sigma_2^2}{\sigma_1^2}\right)^{-1} & \text{disk-like microclusters} \end{cases} \tag{35}$$

in which the terms on the right side of eqn (35) represent the critical nucleation numbers of the solute atoms/particles for the corresponding geometrical configurations of the microclusters formed in an infinite system. It is evident that the variation of the auxiliary parameter, χ, with n, N_1 and N_2 represents the effects of n, N_1 and N_2 on the concurrent nucleation of microclusters of the same shape and size in a finite liquid droplet, and the auxiliary parameter, χ, is independent of the geometrical configurations of the microclusters.

Numerical illustration

As an example of numerical illustration, we consider the nucleation of glucose in an aqueous droplet at 20 °C. We assume that the microclusters formed in the aqueous droplet are present in a spherical shape of r in radius. eqn (18) becomes

$$\begin{aligned}\Delta_m\Psi &= -RT\ln\left(1-(1-x)\frac{nm}{N_1}\right)\\ &\quad+\frac{x}{1-x}RT\ln\left(\frac{1}{x}\cdot\frac{x-(1-x)nm/N_1}{1-(1-x)nm/N_1}\right)\\ &\quad-\frac{nm}{N_1}\Delta_m\Theta+\frac{nN_a}{N_1}4\pi r^2\sigma_m\end{aligned}\tag{36}$$

The solubility of glucose in water at 20 °C is 47.8 g in 100 g of solution,[28] and the molecular weight of glucose is 180.156 g mol^{-1} as reported by Sigma-Aldrich. Using the results given by Van Hook and Kilmartin[28] in the study of a solid-saturated solution of D-glucose in water, we approximate 84 mJ m^{-2} as the interface energy between a glucose microcluster and the glucose-saturated aqueous solution. It is well known that the dissolution of glucose in water is an endothermic process, and the heat of solution is 11 kJ mol^{-1},[29,30] *i.e.*, $\Delta_m\Theta \approx$ 11 kJ mol^{-1}. Using the molecular weight (180.156 g mol^{-1}) and density (1.54 g cm^{-3}) of glucose, the molar volume of glucose is found to be 116.98 cm^3 mol^{-1}.

For the droplet-based microreactors in microfluidic systems, the droplet size can be in a range of 2 to 1000 μm.[31] Here, a size of 2 μm is assumed for a droplet of an aqueous solution of glucose. For a supersaturated droplet of 2 μm in diameter with a degree of supersaturation 2 times the solubility of glucose in water at 20 °C (47.8 g in 100 g of solution), the numbers of water molecules and glucose molecules are calculated to be 6.438 × 10^{10} and 1.164 × 10^{10}, respectively, under the assumption that the volume of the droplet is approximately equal to the summation of the volumes of water and glucose molecules. Note that the volume of the droplet is generally less than the summation of the volumes of water and glucose molecules, *i.e.*, there is a volume contraction. Using the above numerical values, we calculate the free energy per mole of the solvent, $\Delta_m\Psi$. Fig. 2 shows the variation of the change of the free energy per mole of the solvent, $\Delta_m\Psi$, with the size of the microclusters for different numbers of microclusters. It is evident that the maximum change of the free energy per mole of the solvent is an increasing function of the number of nuclei formed in the aqueous droplet. The critical nucleation size also changes with the change of the number of nuclei formed in the aqueous droplet.

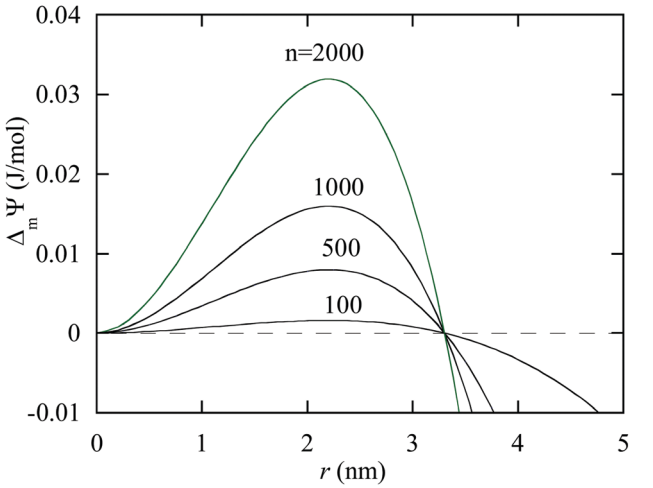

Fig. 2 Variation of the change of the free energy per mole of the solvent with the size of the microclusters for different numbers of microclusters in the aqueous droplet.

It is known that the maximum change of the free energy per mole of the solvent represents the height of the energy barrier needed to be overcome in order to form viable nuclei.[14] Using the results shown in Fig. 2 and/or eqn (36), we calculate the maximum change of the free energy per mole of the solvent and the corresponding critical nucleation size for different numbers of microclusters in the aqueous droplet. We define $\Delta r_c = r_c(n) - r_c(1)$, in which $r_c(n)$ and $r_c(1)$ (= 2.20228 nm) are the critical nucleation sizes with n microclusters and 1 microcluster in the aqueous droplet, respectively. Fig. 3 depicts the variations of Δr_c and the maximum change of the free energy per mole of the solvent with the number of microclusters. According to Fig. 3, both the critical nucleation size and the maximum change of the free energy per mole of the solvent for the concurrent nucleation of n microclusters in the aqueous droplet are increasing functions of the

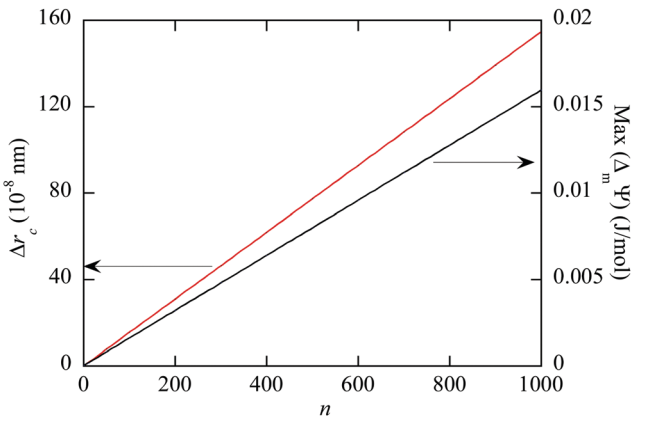

Fig. 3 Variations of the maximum change of the free energy per mole of the solvent and the difference between $r_c(n)$ and $r_c(1)$ with the size of the microclusters for different numbers of microclusters nucleated concurrently in the aqueous droplet.

number of microclusters. That is to say, the higher the number of nuclei in the aqueous droplet, the larger the energy barrier for the concurrent nucleation of the nuclei in the aqueous droplet. According to eqn (36), the effect of the number of microclusters on the critical nucleation behavior is correlated with the number of solvent atoms through the ratio of n/N_1. It is evident that increasing the ratio (*i.e.*, decreasing the droplet size or increasing the number of microclusters) causes an increase of the energy barrier for the nucleation of the nuclei in the droplet.

It needs to be pointed out that there are different approaches available to investigate the nucleation behavior, such as the stochastic method,[32] fluctuating hydrodynamics,[33] density functional theory,[34] and molecular dynamics simulations.[35] Wedekind *et al.*[35] used molecular dynamics simulations to analyze vapor–liquid nucleation with a fixed, total number of particles/atoms and revealed the decrease of the energy barrier for the nucleation of a cluster with the increase of the total number of particles/atoms. The decreasing trend of the energy barrier with the increase of the total number of particles/atoms is qualitatively in accord with the results presented in Fig. 2 and 3. Note that they only considered the nucleation of a single cluster of the same material, which is different from the nucleation of multi-microclusters of solute particles/atoms studied in this work. However, the computational cost and/or the lack of the interaction potential between solvent particles/atoms and solute particles/atoms have hindered the applications of most of these methods in studying the concurrent nucleation of multi-microclusters.

Summary

In summary, we have derived the changes of the Gibbs free energy and the Helmholtz free energy for a liquid droplet of a finite, binary system, in which multiple microclusters can be formed concurrently. Both the free energies are dependent on the number of microclusters formed and the interface energy between the microclusters and the solution in the droplet. Realizing that it is impossible to maintain constant pressure or constant volume of the liquid droplet during the nucleation of the microclusters and the possibly small changes in the pressure and/or the volume, the change of the free energy, which can be approximated as a first order approximation of both the Gibbs free energy and the Helmholtz free energy, has been introduced. Using the change of the free energy with constant interface energy, we have obtained the critical nucleation number of the solute atoms/particles of the nuclei formed in the liquid droplet for three different geometrical shapes of sphere, disk and cube. The critical nucleation number is dependent on the ratio of the number of nuclei to the number of solvent atoms in the liquid droplet for all three geometrical shapes. The numerical calculation of the critical nucleation size for the nucleation of spherical nuclei has revealed that both the critical nucleation size and the maximum change of the free energy per mole of the solvent for the concurrent nucleation of n microclusters in the aqueous droplet are increasing functions of the number of microclusters.

List of variables

$f(\sigma_m)$	Interface energy
F	Helmholtz free energy
G_{init}	Gibbs free energy of the liquid droplet in the supersaturated state
G_{final}	Gibbs free energy of liquid droplet with n microclusters
G_l	Gibbs free energy of liquid droplet without contribution from microclusters and interfaces between microclusters and solution in liquid droplet
k	Boltzmann constant
m	Number of solute atoms/particles in a microcluster
m_c	Critical nucleation number of solute atoms/particles
n	Number of microclusters
N_1	Numbers of solvent atoms
N_2	Numbers of solute atoms
N_a	Avogadro constant
p	Pressure in liquid droplet
p_i, p_f	Pressures in liquid droplet in the supersaturated state and nucleation state, respectively
p_m	Pressure in microclusters
p_0	Pressure in immiscible liquid medium
r_0	Radius of liquid droplet
r_f	Radius of liquid droplet in the nucleation state
T	Absolute temperature
V_0, V_m	Volumes of liquid droplet and an individual microcluster, respectively
x	Atomic fraction of solute atoms/particles
y	Atomic fraction of solute atoms/particles dispersed in solvent in the nucleation state
μ_1^0	Chemical potential of pure solvent atoms in the standard state
μ_2^0	Chemical potential of pure solute atoms in the standard state
μ_1	Chemical potential per solvent atom in the supersaturated state
μ_2	Chemical potential per solute atom in the supersaturated state
μ_m	Chemical potential per solute atom in the microcluster
γ_1	Activity coefficient for solvent atoms in the droplet
σ_i^s	Specific interface tension between the liquid droplet in the supersaturated state and the immiscible liquid medium
σ_f^s	Specific interface tension between liquid droplet in nucleation state and immiscible liquid medium
σ_{pure}	Interface tension of pure solvent
σ_m	Specific interfacial energy for interface between microcluster and solution in the nucleation state
Ω	Molar volume of solute atoms/particles
Γ	Surface excess
$\Delta_m\Psi$	Change of free energy per mole of solvent

Conflicts of interest

There are no conflicts to declare.

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