A Model of Liquid-phase Homogeneous Nucleation in a System Containing Seed Particles

Yasuo Kousaka, Toshiyuki Nomura, Shinji Hasebe and Ken Tanaka
Chemical Engineering Department, Osaka Prefecture University*
Manuel Alonso
National Center of Metallurgical Research, Avda Gregorio del Amo**

Abstract

This paper deals with particle formation by homogeneous nucleation in a system containing seed particles. A model of homogeneous nucleation previously developed by the present authors is here extended to include the effect of the presence of seed particles. To this end, the cell model upon which the original model was based has been modified to account for the random distribution of the inter-particle distances in the medium. Liquid-phase experiments, in which particles have been generated by a chemical reduction method with varying number concentrations of seed particles and generation rates of precursor monomers, have confirmed the validity of the model. The proposed model enables determination of the operating conditions where 1) homogeneous nucleation is predominant, 2) particle growth is predominant, and 3) homogeneous nucleation and particle growth coexist.

1. Introduction

In order to selectively promote the enlargement of particles present in a medium by means of precursor monomer nucleation onto their surfaces, it is necessary to avoid the formation of new particles by self-nucleation. Presently, however, there is no theory for determining under which conditions self-nucleation is suppressed. We have recently developed, and successfully verified, a new model of homogeneous nucleation in the absence of seeds. The objective of this paper is to extend this analysis to account for the effect of the presence of seeds on new particle formation by self-nucleation. The predictions of the proposed model will then be compared with experimental results obtained for liquid-phase particle formation by a chemical reduction method.

2. Theory

2.1 Conditions for Self-Nucleation in the Presence of Seed Particles

In our previous investigation we arrived at the following relationship between the number concentration $n^*$ of nucleated particles and the critical monomer generation rate $G^*$:

$$G^* = 4\pi r^* D C^* n^*.$$  \hspace{1cm} (1)

In this expression, $r^*$ is the radius of the critical nucleus ($r^*=1$ nm), $D$ the diffusion coefficient of monomers (atoms or molecules of the precursor material), and $C^*$ the critical saturation concentration of monomers, i.e. the minimum concentration required for the appearance of new nuclei. When the particle concentration in the system is $n^*$, the monomer generation rate $G$ must be larger than $G^*$ in order to have further particle formation by self-nucleation. Thus, when the number of nucleated particles has become so large that $G < G^*$, homogeneous nucleation stops, no new nuclei can be formed, and the particle number concentration remains constant thereafter.

When seed particles of radius $r_p$ and number concentration $n_p$ are present in the medium, we can write an expression similar to the above:

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* 599-8531 Sakai, Japan
** 8, 28029 Madrid, Spain
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Equating equations (1) and (2) yields

\[ n^*/n_p = R, \quad R = r_p/r^*. \]  

(3)

Therefore, the attainable number concentration of nucleated particles in a system without seeds is \( R \) times that in a system with seeds, other conditions being equal. The reason is that the depletion rate of monomers per seed is \( R \) times larger than the depletion rate per nucleus.

When \( G > G_p \), the depletion of monomers by seeds is low enough so that \( C > C^* \) and new particles can be formed by homogeneous nucleation. In this case, monomers are used for new particle formation as well as for particle growth, and hence we can write

\[ G = G_p + G^* = 4\pi DC^* r^*(Rn_p + n^*). \]  

(4)

In these circumstances, the number concentration of nucleated particles and the total number concentration of particles become

\[ n^* = \frac{G}{4\pi r^* DC^*} - Rn_p, \]  

(5)

\[ n_T = n^* + n_p = \frac{G}{4\pi r^* DC^*} + (1 - R)n_p, \]  

(6)

respectively. Equations (5) and (6) are valid when \( G > G_p \), and cannot be used for the reverse case of \( G < G_p \). Obviously, in the latter situation no new particles can be formed by self-nucleation. Clearly, the condition required for new particle formation by homogeneous nucleation \((n^* > 0)\) is readily obtained from equations (4) or (5) as

\[ G > 4\pi DC^* r^* Rn_p. \]  

(7)

This implies that homogeneous nucleation is suppressed when the number concentration of seed particles is larger than \( 1/R \) \((< 1)\) times the attainable number concentration of nucleated particles in a system without seeds. It further follows from equation (7) that the conditions for homogeneous nucleation suppression depend essentially on the monomer diffusion coefficient, the critical supersaturation concentration of monomers, the size and number concentration of seed particles, and the conditions under which monomer generation takes place (temperature, reaction rate).

**Figure 1** illustrates the variation with reaction time of variables such as the seed radius \( r_p \), the radius of the nucleated particles \( r^* \), the total number concentration of particles \( n_T \), the monomer concentration \( C \), and the monomer concentration \( C_m \) that would result if neither nucleation nor particle growth had taken place. **Figure 1 (a)** describes what happens when \( G < G_p \), that is, when no particles can be formed by self-nucleation because the monomers are consumed solely in seed particle growth, thereby always keeping the monomer concentration below the critical concentration \( C^* \). **Figure 1 (b)** corresponds to \( G > G_p \), that is, when conditions are favorable to new particle formation by homogeneous nucleation. The time \( t^* \) at which the monomer concentration in the liquid medium attains the critical value \( C^* \) is the starting point of self-nucleation. During a certain time interval \( \Delta t \) the monomer concentration is still high enough to produce new particles; at the same time, however, the rate of monomer depletion by diffusion toward particle surfaces steadily increases as new particles are being formed. Thus a time \( t^* + \Delta t^* \) is reached at which the depletion rate has become so large that the monomer concentration in the medium falls below the critical value \( C^* \), stopping homogeneous nucleation.
ation. From this point on the generated monomers are consumed exclusively in particle growth, until the monomer concentration finally attains the saturation value \( C_0 \).

Consider first the absence of seed particles from the system. When the number concentration of nucleated particles is \( n_0^* \), the critical monomer generation rate \( G_0^* \), above which new particles can be formed in the absence of seeds, is given by

\[
G_0^* = 4\pi r^* DC^* n_0^*.
\]

(This is the same as equation (1) except that we have attached a subscript 0 to the appropriate variables to indicate that they refer to a condition in which seeds are absent from the system.)

If, under the same operating conditions, seed particles (radius \( r_p \), number concentration \( n_p \)) are also present in the medium, we can use equation (4) with \( G_0^* \) instead of \( G \), and solve for the number concentration of nucleated particles, resulting in

\[
n_0^* = 1 - R \frac{n_p}{n_0^*}.
\]

The total number of particles thus becomes

\[
\frac{n_T}{n_0^*} = \frac{n_0^*}{n_0^*} + \frac{n_p}{n_0^*} = 1 + \frac{n_p}{n_0^*} (1 - R)
\]

Equations (9) and (10) are plotted in Figure 2. Consider, for instance, the curve for the seed-to-nucleus size ratio \( R = 100 \): when the seed number concentration is such that \( n_p/n_0^* > 10^{-2} \), no new particles can be formed by homogeneous nucleation, but as the seed number concentration is reduced, the total number concentration of particles \( n_T \) gradually approaches the limiting value \( n_0^* \), which corresponds to a system without seeds.

### 2.2 Modification of the Cell-Model to Account for the Presence of Seeds

So far, the model for simultaneous homogeneous and heterogeneous nucleation has been based on our original development using a cell-model with constant cell radius \( b_1 \). However, a modification of the cell-model is necessary in order to reproduce the experimental results of nucleation in the presence of seeds. The constant-size cell model assumes that all the particles are equally spaced. Actually, the particles are randomly distributed in the medium, so that the distance between neighboring particles follows a certain distribution law. As illustrated in Figure 3, monomers generated in regions where the seeds are separated by very small distances are depleted through condensation onto seed surfaces. Conversely, new nuclei can only be formed in those places where the distance between particles is larger. Therefore, one must somehow consider the random distribution of seeds in the medium in order to arrive at a more realistic description of the nucleation process.

The cell-model modification we propose is to assume that, contrary to the above equations, new nuclei can still be formed (i.e. \( C > C^* \)) even when \( G < G_0^* \), but only in a fraction \( v^* \) of the total number of cells. Hence, the number concentration of self-nucleated particles can be written as \( v^* n_0^* \) when the seed concentration is so large that \( G < G_0^* \). An estimation based on kinetic theory arguments led to a value of \( v^* = 0.16 \) for the number fraction of cells where homogeneous nucleation can occur.

Accordingly, the total number concentration of particles (seeds plus self-nucleated) should be rewritten as

\[
\frac{n_T}{n_0^*} = \frac{n_0^*}{n_0^*} + \frac{n_p}{n_0^*} = \begin{cases} 
1+(1-R) \frac{n_p}{n_0^*} & \text{for } Rn_p < n_0^* (1-v^*) \\
v^* + \frac{n_p}{n_0^*} & \text{for } Rn_p > n_0^* (1-v^*)
\end{cases}
\]

Fig. 2 Relationship between total number concentration of particles \( n_T \) and number concentration of seeds \( n_p \) as a function of the seed-to-nucleus size ratio \( R \)

Fig. 3 Effect of the random spatial distribution of seeds on the monomer concentration profile in their vicinity
Equation (11) is plotted in Figure 4 for several values of the seed-to-nucleus size ratio $R$. According to the cell-model modification just introduced, homogeneous nucleation is never completely suppressed, no matter how large the seed number concentration is, although for quite high seed concentrations the relative importance of self-nucleation is certainly insignificant.

3. Experimental Method

Silver experimental particles were generated by the liquid-phase chemical reduction reaction

$$4\text{AgNO}_3 + \text{N}_2\text{H}_4 \rightarrow 4\text{Ag} + \text{N}_2 + 4\text{HNO}_3$$

Equation (12)

Three solutions were prepared: (A) 0.2 g of sodium polyacrylate in 1 l of ultrapure water, (B) silver nitrate in ultrapure water, and (C) hydrazine in ultrapure water. The solution (C) was prepared with an amount of hydrazine larger than required by stoichiometry. 25 ml of each solution were placed in separate beakers in a water bath at 293 K. First, Ag seed particles were generated by pouring the solutions B and C simultaneously into a beaker containing solution A under agitation (particles obtained: diameter 0.3 μm, geometric standard deviation 1.5, number concentration $3 \times 10^{17}$ m$^{-3}$); the number concentration of seed particles could then be changed at will by adding the required amount of ultrapure water. The solution containing the seed particles called D. In order to modify the size of the silver seed particles, 25 ml of solution B was added to 25 ml of solution D under agitation. Two types of experiments were then carried out: 1) varying the concentration of silver nitrate in solution B, thereby modifying the monomer generation rate $G$ (this rate is proportional to the concentration of silver nitrate), and 2) varying the size of the seed particles, thereby modifying the depletion rate of monomers by diffusion toward the particles' surfaces. Furthermore, in the type 1) experiments we employed different seed particle sizes, which were prepared by adding to solution D (diameter 0.3 μm, geometric standard deviation 1.5, number concentration $3 \times 10^{17}$ m$^{-3}$) a solution of high-concentration silver nitrate. Using this procedure we were able to obtain seeds with average diameters 0.5 and 1.0 μm, both of which had a geometric standard deviation of 1.5. The reason for using ultrapure water in the experiments was to prevent the presence of contaminants that could act as undesired nucleation seeds. The zeta potentials of the solutions were measured before and after particle generation by nucleation. The measured values were always above 20 mV, which means that particle coagulation did not occur in the medium during the experiments. The number concentration and size of the generated silver particles were measured following the same procedure described in our previous works.\textsuperscript{1,2}

4. Results and Discussion

Figure 5 shows the results of the experiments carried out by adding silver nitrate solutions of different concentrations to a suspension of 0.3 μm seed particles. As explained above, varying the concentration of silver nitrate is equivalent to modifying the monomer generation rate $G$. The straight dotted line in this Figure corresponds to the extreme case in which homogeneous nucleation does not occur at all, so that the total number concentration of particles in the system is simply equal to the number concentration of seeds,
i.e., monomers are only used for seed growth ($n^*=0$). From our previous experiments\(^1\) we know the number concentration $n^*_0$ of nucleated particles in the absence of seeds as a function of the concentration of silver nitrate in the solution. The curves plotted in Figure 5 were calculated with equation (11) using the previously known values of $n^*_0$, the theoretically estimated value of the fraction of cells of sizes larger than the average ($\phi^* = 0.16$), and the seed-to-nucleus size ratio $R = r_p/r^* = 150$ ($r_p = 150$ nm, $r^* = 1$ nm). As seen in the figure, when the seed number concentration $n_p$ is very low, the total number concentration of particles in the system is practically constant, independent of $n_p$. The reason is that when $n_p$ is very low, the generation rate of monomers $G$ is much larger than the monomer depletion rate by diffusion toward seeds ($G = G_0$) and homogeneous nucleation is predominant. At the other extreme, when the seed number concentration is very high, homogeneous nucleation is practically suppressed. At intermediate levels of seed concentration both mechanisms – self-nucleation and particle growth – coexist. The existence of these three different situations, namely, predominant homogeneous nucleation, coexistence of nucleation and growth, and predominant particle growth, has been also verified in gas-phase systems.\(^3\) According to the theoretical curves plotted in Figure 2, homogeneous nucleation is suddenly suppressed at a certain value of the seed number concentration, and this causes a sharp decrease in the total number of particles in the system. This is, however, in clear contradiction to the experimental data plotted in Figure 4. Modification of the cell-model to account for the number fraction of cells with sizes larger than the average ($\phi^* = 0.16$) produces a theoretical picture markedly different from that of Figure 2. That is, now the suppression of self-nucleation with an increasing number concentration of seeds is not a clear-cut phenomenon, but rather one which takes place gradually in such a manner that, in fact, homogeneous nucleation is never completely suppressed. The reason for this is found in the random spatial distribution of seeds in the medium whereby some interparticle voids are sufficiently large to permit the formation of new nuclei. This is also observed in Figure 6, which plots the same data as Figure 5 but in non-dimensional form.

Figure 7 shows the results obtained in the experiments carried out at a constant monomer generation rate (i.e., a constant concentration of the silver nitrate solution) and a varying seed particle size. The diameters of the seeds used were 0.3, 0.5, and 1.0 $\mu$m, giving seed-to-nucleus size ratios $R$ of 150, 250 and 500.
respectively. The straight line has the same meaning as explained for Figure 5. The same data is plotted in non-dimensional form in Figure 8. From any of these two figures, we observe again the presence of three regions according to the level of seed particle number concentration: a region with predominant homogeneous nucleation and practically no particle growth (low \(n_p\)), a region with predominant particle growth and insignificant new particle formation by self-nucleation (high \(n_p\)), and an intermediate region where both phenomena coexist.

In summary, we have seen that the data obtained from two different types of nucleation experiments in the presence of seeds can be accurately predicted with the proposed modified-cell model, in which the random size distribution of the empty space between seeds has been taken into account.

5. Conclusions

Based on our previous work,\(^1\) we have developed a practical model of homogeneous nucleation in the presence of seed particles, including the effect of the randomly-sized empty space among particles. We demonstrated that the model predictions are in excellent agreement with the results of experiments performed with varying monomer generation rates, and sizes and concentrations of seed particles. The model allows assessment of the operating conditions under which 1) homogeneous nucleation is predominant, 2) particle growth is predominant, and 3) both phenomena, self-nucleation and particle growth, coexist.

| Nomenclature                  | Unit               |
|-------------------------------|--------------------|
| \(b\) : radius of unit cell   | \([m]\)            |
| \(C\) : monomer concentration | \([kg/kg\text{-liquid}]\) |
| \(C_m\) : monomer concentration without nucleation | \([kg/kg\text{-liquid}]\) |
| \(C_0\) : critical monomer saturation concentration | \([kg/kg\text{-liquid}]\) |
| \(C^*\) : critical monomer supersaturation concentration | \([kg/kg\text{-liquid}]\) |
| \(D\) : monomer diffusion coefficient | \([m^2/s]\) |
| \(G\) : monomer generation rate | \([kg/(kg\text{-liquid}\cdot s)]\) |
| \(G_p\) : monomer generation rate with seed particles | \([kg/(kg\text{-liquid}\cdot s)]\) |
| \(G^*\) : monomer generation rate when \(n=n^*\) | \([kg/(kg\text{-liquid}\cdot s)]\) |
| \(G_{0^*}\) : monomer generation rate without seeds | \([kg/(kg\text{-liquid}\cdot s)]\) |
| \(n_p\) : number concentration of seed particles | \([m^{-3}]\) |
| \(n_T\) : total number concentration of particles | \([m^{-3}]\) |
| \(n^*\) : number concentration of self-nucleated particles | \([m^{-3}]\) |
| \(n_{0^*}\) : number concentration of self-nucleated particles without seeds | \([m^{-3}]\) |
| \(R\) : seed-to-nucleus size ratio | \([-]\) |
| \(r_p\) : radius of seed particles | \([m]\) |
| \(r^*\) : radius of critical nucleus | \([m]\) |
| \(t\) : time | \([s]\) |
| \(t^*\) : time at which \(C=C^*\) | \([s]\) |
| \(v^*\) : number fraction of cells with radius larger than the average | \([-]\) |

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Author's short biography

Yasuo Kousaka
The author is Professor of Chemical Engineering Department at Osaka Prefecture University since 1979. His major research interests are dynamic behavior of aerosol particles, sizing techniques of aerosol particles and powders, dispersion of aggregate particles in air and water, and particle formation by homogeneous and heterogeneous nucleation. He is currently the vice president of the Association of Powder Process Industry and Engineering, Japan.

Toshiyuki Nomura
The author received his B.S. and M.S. degrees from Kyoto University in 1993 and 1995, respectively. He earned his Ph.D. degree in Chemical Engineering in 1999 from Osaka Prefecture University. He is Research Instructor of Chemical Engineering Department at Osaka Prefecture University since 1996. His major research interests are particle formation by homogeneous and heterogeneous nucleation, dynamic behavior of aerosol particles and electrostatic characteristics of powder.

Manuel Alonso
The author received his B.S. and M.S. degrees from the University of Malaga, Spain, in 1984 and 1985, respectively. He earned his Ph.D. degree in Chemical Engineering in 1991 from Osaka Prefecture University, where he later stayed as a Research Associate in 1994-1996. Since 1996 he is a tenured scientist at the National Center of Metallurgical Research in Spain. His research activities have ranged from Powder Technology in the past (powder mixing and coating, particle packings) to Aerosol Science at present (aerosol particle formation, coagulation, charging, size measurement, and filtration).