Grain Formation through Nucleation Process in Astrophysical Environment

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General picture of grain formation is presented based on the nucleation theory. Grain formation process is described by a growth equation of grain radius and an equation of monomer consumption due to the growth of grains. These equations are characterized by two parameters. One depends on the physical conditions of the system and the other reflects the nature of grain materials. An overall feature of the grain formation process is illustrated by the use of an analytic expression of the solutions. After the vapor cools down to the saturated state, a waiting time is necessary until the grain formation begins effectively. Size distribution is relatively sharp in general. The representative size is closely related to the parameter which depends on the physical conditions. Growth by coalescence is not effective until the monomer sticking process is almost completed. The results are applied to the condensation in the primordial solar nebula. It is shown how the picture based on the chemical equilibrium calculations should be modified.

§ 1. Introduction

Grain formation has been studied by many people in a wide range of physical conditions especially in connection with astrophysical problems. Much work has been done on the formation of interstellar grains to make their origins clear as well as on their optical properties on the basis of the interstellar extinction curve to investigate their composition and sizes. While the condensation in the primordial solar nebula has been studied in relation to the chemical history of meteorites. The species of condensates and their condensation sequence in the cooling gas of cosmic composition have been known based on the chemical equilibrium calculations.

We shall describe in this paper a general picture of grain formation based on nucleation theory.

Among various quantities concerning grain formation which we can derive, sizes of grains have an important meaning. They reflect faithfully the physical conditions such as the pressure and the cooling rate for the gas in which the grain formation occurs. Therefore the sizes of interstellar grains guessed by their optical properties can be connected with their origins. As to the condensation in the primordial solar nebula, our method provides a clue to infer the cooling rate of the gas by noticing the grain sizes of minerals contained in the primitive meteorites.

Another point which we predict is that a supercooling state must be realized for condensation to occur effectively. The condensation sequences based on the chemical equilibrium calculations will require modifications.
We shall derive the basic equations and a similarity relation in § 2. In § 3, an overall feature of grain formation process is illustrated. Growth by coalescence is investigated briefly in § 4. Discussion focused on the condensation in the primordial solar nebula is presented in § 5.

§ 2. Basic equations

Let us consider a cooling gas which contains a vapor of condensable materials. When the partial pressure of the vapor reaches the saturated vapor pressure at temperature $T_e$, we call it equilibrium temperature instead of condensation temperature to avoid confusion.

Below the equilibrium temperature $T_e$, nucleation process begins to occur. Nuclei grow into grains by the sticking of the vapor molecules, which is called monomers hereafter. Now let $r(t, t')$ be a radius of a grain nucleated at time $t'$ but observed at time $t$. The growth of radius of grain $r$ is described by

$$\frac{dr}{dt} = \alpha \Omega \langle v \rangle c_1(t), \quad (2 \cdot 1)$$

where $\alpha$, and $\Omega$ are the sticking probability and the volume of monomer respectively, $\langle v \rangle = \sqrt{kT/2\pi m}$ is the mean thermal velocity of monomers, $m$ being the mass of monomer and $k$, the Boltzmann constant, and $c_1(t)$ is the monomer concentration at time $t$. Here we put $t=0$ when the vapor temperature $T$ becomes the equilibrium temperature $T_e$. Since $\langle v \rangle$ is less sensitive to temperature and almost constant in the relevant time interval, we shall regard it as a constant hereafter. We have also neglected in Eq. (2·1) the size decrease by evaporation because the nuclei are stabilized soon after they are nucleated due to the increase of the supersaturation.

As the grains grow with time, the monomers are consumed. The monomer depletion to form nuclei is negligible. Then the monomer concentration $c_1(t)$ is described by

$$c_1(t) = c_1(0) - \int_0^t J(t') \frac{4\pi}{3\Omega} r(t, t')^3 dt'. \quad (2 \cdot 2)$$

The steady state nucleation rate $J$, the number of nuclei formed per unit time per unit volume, is given according to the classical homogeneous nucleation theory\(^n.0\) by

$$J(t) = \alpha \Omega \left( \frac{2\sigma}{\pi m} \right)^{1/2} c_1(t)^3 \exp \left\{ -\frac{4\mu^2}{27 \ln S(t)} \right\}, \quad (2 \cdot 3)$$

where $S$ is the supersaturation ratio and $\sigma$ is the surface tension of condensate. In Eq. (2·3), $\mu$ is defined by

$$\mu = \frac{4\pi \sigma a_0^2}{kT} \cdot \quad (2 \cdot 4)$$

\(n.0\)
where \( a_0 \) is a radius of the monomer. Since \( \mu \) is less sensitive to temperature compared with \( S \), we use the \( \mu \) value at the equilibrium temperature \( T_e \).

The supersaturation ratio \( S \) is a very sensitive function of temperature. If we neglect the monomer depletion due to the growth of grains, the supersaturation ratio \( S \) varies with temperature as \( S = (T/T_e) \exp \left( (h/k) \left( 1/T - 1/T_e \right) \right) \), where \( h \) is the molecular latent heat. Since the temperature \( T \) does not vary much in the relevant time interval of grain formation, we can approximate \( T \) as a linear function of time \( t \). Then the supersaturation ratio is given, including the monomer depletion, by

\[
S(t) = \frac{c_1(t)}{c_1(0)} \exp \left( \frac{t}{\tau_{\text{sat}}} \right).
\]

Here \( \tau_{\text{sat}} \) is given by

\[
\tau_{\text{sat}} = \frac{\tau_r}{h/kT_e - 1},
\]

and \( \tau_r \) is a cooling time scale of the vapor, which is defined by

\[
\tau_r = \left| \frac{d \ln T}{dt} \right|^{-1} \left( \tau = T_e \right).
\]

Equations (2.1) and (2.2) together with Eqs. (2.3) \( \sim \) (2.7) are the basic equations of grain formation.

Now we introduce the other characteristic time, the mean collision interval of monomers \( \tau_{\text{coll}} \), as

\[
\tau_{\text{coll}} = (a_0 c_1(0) 4\pi a_0^2 \langle v \rangle)^{-1}
\]

and define an important parameter \( A \) by

\[
A = \frac{\tau_{\text{sat}}}{\tau_{\text{coll}}}.
\]

We transform the time \( t \), the monomer concentration \( c_1(t) \) and the radius of a grain \( r \) as follows:

\[
x = t/\tau_{\text{sat}},
\]

\[
y = c_1(t)/c_1(0)
\]

and

\[
\rho = 3r/a_0 A.
\]

The basic equations (2.1) and (2.2) are transformed, respectively, into

\[
d\rho/dx = y
\]

and

\[
1 - y = \frac{1}{81} \sqrt{\frac{\mu}{\pi}} A^4 \int_0^x \exp \{ g(x') \} \rho(x, x') dx',
\]

where

\[
a_0 \theta = a_0 \theta_0 - a_0 \theta_0 (1/T - 1/T_e)
\]

and

\[
S = (T/T_e) \exp \left( (h/k) \left( 1/T - 1/T_e \right) \right).
\]
where
\[ g(x) = 2 \ln y(x) - 4\mu^0/27(x + \ln y(x))^2. \] (2.15)

It should be noted that the basic equations (2.13) and (2.14) with (2.15) include only the two parameters \( A \) and \( \mu \). On account of this, we can see that a similarity relation holds in grain formation processes in various situations. Namely, features of grain formation processes are the same under the same values of \( A \) and \( \mu \) in terms of the nondimensional variables defined by Eqs. (2.10)~(2.12).

The parameter depends on the physical conditions of the relevant system, such as the monomer concentration and the cooling rate, whereas \( \mu \) reflects the nature of grain material especially on its surface tension.

The crude values of \( \mu \) for some typical grain materials and those of \( A \) for various astrophysical and physical systems are listed in Tables I and II.

**Table I.** Thermodynamical parameters of some grain materials.

<table>
<thead>
<tr>
<th>Species</th>
<th>( T_e (K) ) ( ^{(b)} )</th>
<th>( h/kT_e ) ( ^{(a)} )</th>
<th>( \sigma ) (erg/cm(^2))</th>
<th>( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicate</td>
<td>( \sim 1000 )</td>
<td>60( ^{(a)} )</td>
<td>875( ^{(b)} )</td>
<td>20</td>
</tr>
<tr>
<td>iron</td>
<td>( \sim 1000 )</td>
<td>50( ^{(a)} )</td>
<td>1800( ^{(b)} )</td>
<td>30</td>
</tr>
<tr>
<td>graphite</td>
<td>( \sim 2000 )</td>
<td>40( ^{(b)} )</td>
<td>1000( ^{(b)} )</td>
<td>7</td>
</tr>
<tr>
<td>water</td>
<td>( \sim 300 )</td>
<td>20( ^{(b)} )</td>
<td>70( ^{(b)} )</td>
<td>2</td>
</tr>
</tbody>
</table>

3), 5)~9): Reference number.
a) For cosmic abundance gas (Grossman, Ref. 2).
b) Since the saturated vapor pressure which determines \( T_e \) is a very sensitive function of temperature and does not strongly depend on the pressure and the chemical composition, we adopt above values for a rough estimate.

**Table II.** Values of \( A \) and of relevant physical parameters of some objects.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \sigma_0 (cm^{-3}) )</th>
<th>( \tau (sec) )</th>
<th>( A ) ( ^{(a)} )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>novae</td>
<td>silicate</td>
<td>( 5 \times 10^{14} ) to ( 5 \times 10^{18} )</td>
<td>( 9 \times 10^6 )</td>
<td>0.9 ( \sim ) 90</td>
</tr>
<tr>
<td>supernovae</td>
<td>graphite</td>
<td>( \sim 10^8 )</td>
<td>( \sim 10^7 )</td>
<td>2 ( \times ) 10^4</td>
</tr>
<tr>
<td>cloud chambers</td>
<td>water</td>
<td>( 5 \times 10^{17} )</td>
<td>( 1 \times 10^{-1} )</td>
<td>5 ( \times ) 10^4</td>
</tr>
<tr>
<td>steller atmospheres</td>
<td>graphite</td>
<td>( 1 \times 10^{11} )</td>
<td>( 3 \times 10^7 )</td>
<td>6 ( \times ) 10^6</td>
</tr>
<tr>
<td>(carbon stars)</td>
<td>graphite</td>
<td>( 4 \times 10^{10} ) to ( 4 \times 10^{10} )</td>
<td>( 4 \times 10^7 )</td>
<td>( 3 \times 10^10 ) to ( 3 \times 10^9 )</td>
</tr>
<tr>
<td>primordial solar</td>
<td>silicate</td>
<td>( \sim 7 \times 10^{11} ) (at 0.1 au)</td>
<td>( 3 \times 10^7 )</td>
<td>( 3 \times 10^9 )</td>
</tr>
<tr>
<td>nebula</td>
<td>iron</td>
<td>( 2 \times 10^{11} ) (at 1 au)</td>
<td>( 2 \times 10^7 )</td>
<td>( 6 \times 10^6 )</td>
</tr>
</tbody>
</table>

a) We have adopted \( h/kT_e \sim 1 \sim 50 \) except for water. For water, \( h/kT_e \sim 1 \sim 20 \) is adopted.

§ 3. An overall feature of grain formation process

We shall illustrate an overall feature of grain formation by adopting an analytic expression of the solutions of Eqs. (2.13) and (2.14) with good approximations.

Just below the equilibrium temperature \( T_e \), the supersaturation ratio is not...
much larger than unity, and so the nucleation rate is extremely small. Under an approximation of \( y \approx 1 \), Eq. (2.13) gives \( \rho(x, x') = x - x' \). Then integration on the right-hand side of Eq. (2.14) yields the monomer consumption \( 1 - y(x) \) as

\[
1 - y(x) = \frac{1}{216} \sqrt{\frac{\mu}{\pi}} A^4 \frac{e^{-u}}{u^u},
\]

where

\[
a = \sqrt{4/27},
\]

and

\[
u = a^2/x^2.
\]

Here \( u \gg 1 \) holds in this stage.

As the vapor cools further, the nucleation rate increases very rapidly. The time \( x_J \) when the nucleation rate attains its maximum is given by the solution of \( dg(x)/dx = 0 \). Using Eq. (3.1), we obtain the following equation for \( x_J \),

\[
\frac{1}{108} \sqrt{\frac{\mu}{\pi}} A^4 \frac{e^{-u}}{u^u} \approx \left( 1 + \frac{1}{v_J} \right)^{-1},
\]

where \( u_J = a^2/x_J^2 \) and \( v_J = a^2/x_J^2 \). We can replace the right-hand side of Eq. (3.4) by unity approximately since \( v_J \gg 1 \) except for small \( A \) as shown later. The solution of Eq. (3.4) gives the time when the nucleation rate becomes remarkable. The values of \( x_J \) with \( u_J \) and \( v_J \), and the monomer consumption at \( x_J \), \( 1 - y(x_J) \), for a wide range of \( A \) and \( \mu \) are presented in Table III. Both \( u_J \) and \( v_J \) are relatively insensitive to \( A \) and much larger than unity except for small \( A \). Hence Eqs. (3.1) and (3.4) are valid also around \( x = x_J \).

Expanding \( g(x) \) around \( x = x_J \) with the aid of Eqs. (3.1) and (3.4), we have

\[
\exp \{ g(x) \} \approx \exp \{ g(x_J) - 2v_J^2(x - x_J)^2 \},
\]

which has a very sharp maximum at \( x = x_J \) since \( v_J \gg 1 \). Thus the nucleation occurs remarkably in a very short time interval around \( x = x_J \), during which most of the nuclei of grains are formed. It is noted however that the monomer consumption due to the nucleation is only a little except for small \( A \) (see Table III).

After the remarkable nucleation, the monomers begin to decrease appreciably. Using the approximation (3.5), we integrate Eq. (2.14), obtaining an expression for the monomer depletion at \( x \geq x_J \) as

\[
1 - y(x) = \rho(x, x_J)^\beta/\rho_\infty^\beta,
\]

in which we have neglected the monomer depletion for \( x \leq x_J \). In Eq. (3.6), \( \rho_\infty \) is defined by

\[
\rho_\infty^\beta = \frac{1}{81v_J} \sqrt{\frac{\mu}{2}} A^4 \exp \{ g(x_J) \}.
\]
Grain Formation through Nucleation Process

Table III. Relevant quantities of grain formation versus $A$ and $\mu$.

<table>
<thead>
<tr>
<th>$\mu$</th>
<th>$\log A$</th>
<th>$u_J$</th>
<th>$v_J$</th>
<th>$x_J$</th>
<th>$1/2v_J^{a)$}</th>
<th>$\rho_\infty$</th>
<th>$r_\infty^{b)$}</th>
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<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>1.52</td>
<td>0.154</td>
<td>9.87</td>
<td>3.25</td>
<td>2.93</td>
<td>0.98 Å</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.19</td>
<td>0.972</td>
<td>5.34</td>
<td>0.514</td>
<td>0.859</td>
<td>2.86</td>
</tr>
<tr>
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<td>2</td>
<td>11.0</td>
<td>3.00</td>
<td>3.67</td>
<td>0.167</td>
<td>0.405</td>
<td>13.5</td>
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<tr>
<td></td>
<td>3</td>
<td>18.0</td>
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<td>2.87</td>
<td>0.080</td>
<td>0.248</td>
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<td></td>
<td>4</td>
<td>25.6</td>
<td>10.6</td>
<td>2.41</td>
<td>0.047</td>
<td>0.174</td>
<td>580</td>
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<tr>
<td></td>
<td>5</td>
<td>33.6</td>
<td>16.0</td>
<td>2.10</td>
<td>0.031</td>
<td>0.133</td>
<td>4430</td>
</tr>
<tr>
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<td>6</td>
<td>41.9</td>
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<td>0.022</td>
<td>0.106</td>
<td>3.53 $\mu$</td>
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<td>1.72</td>
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<td>0.011</td>
<td>0.066</td>
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</tr>
<tr>
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<td>76.0</td>
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<td>0.009</td>
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<td>1.96 cm</td>
</tr>
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<td>3.44</td>
<td>1.15 Å</td>
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<tr>
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<td>6</td>
<td>45.0</td>
<td>7.91</td>
<td>5.13</td>
<td>0.063</td>
<td>0.198</td>
<td>6.60 $\mu$</td>
</tr>
<tr>
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<tr>
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<td>17.2</td>
<td>4.10</td>
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<td>0.126</td>
<td>4200</td>
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<td>79.3</td>
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<td>0.189</td>
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<td>38.5</td>
<td>3.78</td>
<td>10.2</td>
<td>0.132</td>
<td>0.347</td>
<td>1.16 $\mu$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>46.9</td>
<td>5.08</td>
<td>9.24</td>
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<td>55.3</td>
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<td>72.5</td>
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<td>7.43</td>
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</tr>
<tr>
<td></td>
<td>10</td>
<td>81.2</td>
<td>11.6</td>
<td>7.02</td>
<td>0.043</td>
<td>0.165</td>
<td>5.50 cm</td>
</tr>
</tbody>
</table>

a) $1/2v_J^{a)$}$\cong 1 - y(x_J)$\cong 2x_J$.

b) For $a_0=1$ Å.

Since $y(x)\to 0$ for $x\to \infty$, we have $\rho(x\to \infty, x_J) = \rho_\infty$. That is, $\rho_\infty$ is the final radius of grains nucleated at $x=x_J$, which is the representative size of most grains as well. Equation (3.7) is rewritten by using Eq. (3.4) and $v_J \gg 1$ as

$$\rho_\infty = \left( \frac{3}{4} \sqrt{\frac{2}{\pi}} \right)^{1/3} \frac{a^{2/3}}{u_J}.$$  (3.8)
Inserting Eq. (3.6) to the growth equation (2.13), we have
\[ \frac{d\rho}{dx} = 1 - \rho/\rho_\infty. \]  
(3.9)
Since most of grains are nucleated around \( x=x_J \), we shall integrate Eq. (3.9) from \( x_J \) to \( x \) and obtain
\[ x - x_J = \rho_\infty I(\rho/\rho_\infty), \]  
(3.10)
where \( I(\chi) \) is defined by
\[ I(\chi) = \int_0^x \frac{dt}{1 - t^3} \]
\[ = \frac{1}{6} \ln \frac{1 - \chi^3}{(1 - \chi)^3} + \frac{1}{\sqrt{3}} \tan^{-1} \frac{2\chi + 1}{\sqrt{3}} - \frac{\pi}{6\sqrt{3}}. \]  
(3.11)

Equations (3.6) and (3.10) with (3.11) describe the growth of grains and the monomer depletion for \( x > x_J \).

An example of the solutions is presented in Fig. 1. It is noted that the grain formation does not begin at the equilibrium temperature \( T_\infty(x=0) \) but at a supercooling state. The "waiting time" for the grain formation \( x_J \) is long enough compared with other time intervals, one in which the growth of a grain comes practically to the end and the other in which the remarkable nucleation continues. Generally they are in the ratio of 1: \( \sim 1/10 : \sim 1/100 \).

The supercooling \( \Delta T \) during the waiting time is calculated as
\[ \frac{\Delta T}{T_\infty} = \frac{1}{T_\infty} \int_0^{t_J} \frac{dT}{dt} \, dt \]
\[ \sim \frac{x_J}{h/kT_\infty - 1} \]
\[ = \frac{a/\sqrt{u_J}}{h/kT_\infty - 1}, \]  
(3.12)
where \( t_J \) is the time at the maximum of the nucleation rate. The supercooling
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Fig. 2. Supercooling $\Delta T/T_e$ versus $A$ for $\mu=10$, 20 and 30, where $T_e$ is the equilibrium temperature. Here we adopt $1/kT_e=50$.

$\Delta T/T_e$ is shown in Fig. 2. Since $u_s$ is less dependent on the surface tension $\sigma$ of grain materials, we may consider approximately that $\Delta T/T_e \propto a \propto \sigma^{1/2}$.

Now let us derive formulae concerning a final feature of the grain formation process.

i) final size

The representative final radius $r_\infty$ is considered to be that of grains nucleated at $x=x_r$. From Eqs. (2.12) and (3.8), we obtain

$$ \frac{r_\infty}{a_0} = \frac{A \rho_\infty}{3} = \left( \frac{1}{36} \sqrt{\frac{2}{\pi}} \right) \frac{a^{3/2}}{\omega J} A. \quad (3.13) $$

Figure 3 shows that sizes of grains are insensitive to $\mu$ but determined mainly by the parameter $A$ which depends on the physical conditions of the system.

ii) size distribution

We have shown that most of the nuclei of grains are formed in the short time interval around the maximum of the nucleation rate. The time interval $\Delta x_J$ is expressed by using Eq. (3.5) as

$$ \Delta x_J = \left[ \int_0^\infty (x-x_J)^2 \exp \{ g(x) \} \, dx \right]^{1/2} = 1/2 \omega J. \quad (3.14) $$

Corresponding to this interval, final radii of grains are distributed around $r_\infty$. The width of the distribution in terms of the nondimensional variable $\Delta \rho_\infty$ is
since the monomer depletion is negligible around $x=x_J$ and the growth rate is independent of the radius of grains (Eq. (2.13)). Thus we obtain the width of the size distribution $\delta r_\infty$ by using Eq. (3.8) as

$$\frac{\delta r_\infty}{r_\infty} = \frac{\Delta \theta_\infty}{\sigma_\infty} = \frac{1}{2} \left( \frac{4}{3} \sqrt{\frac{\pi}{2}} \right)^{1/3} \alpha^{1/3} \sigma^{1/2} u_J. \quad (3.16)$$

Since the nucleation rate has a very sharp maximum, the size distribution has a relatively sharp Gaussian-like shape in general, whose relative width $\delta r_\infty/r_\infty$ is found to be less than about 50% for $A > 10^4$.

iii) number density of grains

Number density of grains $N_\sigma$ is given by integrating the nucleation rate $J$ from $t=0$ to infinity. Rewriting Eq. (2.3) as

$$J = \frac{4}{3} r_{\text{sat}} \sqrt{\frac{\mu}{\pi}} c_1(0) \exp\{g(x)\},$$

we find

$$N_\sigma \frac{c_1(0)}{c_1(0)} = \frac{1}{c_1(0)} \int_0^\infty Jdt,$$

$$= 36 \frac{\pi}{2} \left[ \frac{1}{A^2} \right] \frac{\mu}{\pi} c_1(0)^3, \quad (3.17)$$

where we have used Eq. (3.4) with its right-hand side approximated to unity.

§ 4. Growth by coalescence

Grains grow by both monomer sticking and coalescence in general. Precedent theories have not clarified which process is dominant. Our general picture can give a clear answer to the question.

Since the growing grains have been shown to have a relatively sharp Gaussian-like size distribution generally, we assume here that they are of a single size for simplicity. Coalescence will begin to play a major role when the growth rate by grain-grain collision becomes larger than the growth rate by monomer sticking.

Let $n$ be the number of monomers contained in a grain of radius $r$, then the ratio between both the growth rates $\xi$ is expressed by

$$\xi = \frac{\alpha n N_\sigma 4\pi (2r)^2 \langle v \rangle}{\alpha c_1(t) 4\pi r^2 \langle v \rangle}$$

$$= \frac{4\alpha_s N_\sigma}{\alpha_s c_1(t) \sqrt{n}},$$
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where \( \langle v_p \rangle \) is the mean thermal velocity of grains and \( \alpha_p \), the sticking probability for the grain-grain collision. Since the nucleation is remarkable only in the short time interval around the time \( t_\nu \), we may consider \( N_p(t > t_\nu) \approx N_p(t \to \infty) \). Then the conservation of the total number of monomers, i.e., \( n_\infty N_p(t \to \infty) = c_0(0) \), and Eq. (3.6) yield

\[
\xi = \frac{4\alpha_p}{\alpha_s} \frac{1}{\sqrt{n_\infty}} \frac{\sqrt{n/n_\infty}}{1 - n/n_\infty},
\]

where \( n_\infty \) is the number of monomers contained in a grain of final size \( r_\infty \). Since \( n_\infty \gg 1 \) (e.g., \( n_\infty \sim 10^{11} \) for \( r_\infty = 1 \mu \)), \( \xi \) becomes larger than unity only when \( n \approx n_\infty \) unless \( 4\alpha_p/\alpha_s \gg 1 \). Therefore coalescence, if it occurs frequently, will contribute to the growth after the monomer sticking process is almost completed and most of monomers are consumed up.

§ 5. Discussion

Let us focus attention on the condensation in the primordial solar nebula. This problem has been studied in detail based on the chemical equilibrium theory. We shall discuss here new views which result from our kinetic treatment on referring to the chemical equilibrium condensation theory. Analyses of some kinds of meteorites may confirm our views.

(1) We have shown that the final size is determined mainly by the parameter \( \Lambda \) which depends on the physical conditions of the system (Fig. 3). It should be noted that owing to this fact we can get information on the physical conditions where and/or when the grains are formed by noticing their sizes. Among them, the cooling rate of gas, which is not derived from the chemical equilibrium theory, may be estimated in the following way. The grain size yields the corresponding \( \Lambda \) (Fig. 3), which is proportional to the ratio of cooling time scale to the monomer-monomer collision time interval. The latter is calculated if the pressure and the temperature of gas are known. Consequently we obtain the cooling rate of gas.

Therefore if primitive grains which nucleated homogeneously and did not suffer the coalescence and the secondary metamorphism are identified in meteorites, we will be able to estimate the cooling rate of the earliest environment in which the meteorites are formed.

(2) In the chemical equilibrium theory, it has been considered that condensation begins when a vapor cools to the equilibrium temperature which is predicted by the chemical equilibrium calculations. On the other hand we have shown that condensation does not begin at the so-called "condensation temperature" but the "waiting time" arises before it begins effectively, that is, a supercooling state must be realized. Blander and Katz first pointed out this effect but we can investigate it more quantitatively. The temperature at which condensation begins effectively shifts toward the lower side than the "condensation temperature" approximately
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in proportion to the 3/2-th power of the surface tension of grain materials (Fig. 2). The supercooling effect is important in some cases in considering the condensation sequence in the primordial solar nebula.

One of them is concerned with the order of condensation of iron and Mg-silicate which is one of the main parts in the condensation sequence in the solar nebula. According to the chemical equilibrium calculations, iron is considered to condense at higher temperature than forsterite (MgSiO₃) at total gas pressure above about 10⁻⁴ atm due to a difference of the molecular latent heat of these materials. Grossman's equilibrium sequence shows that at total pressure 10⁻³ atm solid iron first appears at 1473K and further cooling leads to an appearance of forsterite at 1444K, at which temperature 46% of the total iron is already condensed. On the basis of these calculations, the following hypothesis is presented: iron which is the precedent condensate accumulates to form cores of the terrestrial planets and Mg-silicate which is the following one accretes on them to form the mantles of the planets. However, the above picture of the condensation sequence will be modified as follows considering the supercooling effect.

We shall adopt here numerical values for total pressure 10⁻¹ atm given by Grossman. As the gas cools to the "condensation temperature" of iron 1473K, the condensation of iron does not begin immediately. Adopting $A \sim 10^8$ and $\mu \approx 30$ for iron (Tables I and II), we obtain $dT \approx 200K$ for $T_e = 1473K$ from Fig. 2. Thus iron begins to condense effectively at about 1270K. While forsterite has smaller surface tension than that of iron, which yields $\mu \approx 20$ (Table I). Then the supercooling $dT$ for forsterite is estimated from Fig. 2 to be about 100K for $T_e = 1444K$, and the effective condensation temperature is about 1340K, at which temperature the condensation of iron is still blocked. Therefore the condensation of Mg-silicate precedes that of iron. The same is true below about 10⁻² atm according to a rough estimate.

Once Mg-silicate grains have condensed, they may act as seed nuclei and lower the nucleation barrier of iron, which will lead to heterogeneous condensation of iron at higher temperature than the effective condensation temperature about 1270K mentioned above. If the above process actually occurs, Mg-Fe-silicate grains will be formed.

It should be pointed out however that this picture depends strongly on the surface tension of grain materials, accurate values of which, especially those of various silicates, are necessary to make it more quantitatively.

(3) Mg-silicate will condense at higher temperature than iron as shown above. We refer again to Grossman's equilibrium calculation, which states as follows. Forsterite appears at 1444K and begins to consume Mg-vapor. The depletion of Mg-vapor blocks the condensation of enstatite (MgSiO₃), which is formed by the reaction of forsterite with the gas after it cools to 1349K. According to the view derived from our kinetic treatment, however, Mg-silicate will not necessarily condense as forsterite. Because due to the supercooling effect Mg-vapor is not depleted
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above about 1340K which is the effective condensation temperature of forsterite. In this case the "condensation temperature" of enstatite is, according to Grossman, 1422K, which is sufficiently close to that of forsterite. In addition this temperature is higher enough compared with the effective condensation temperature of forsterite. Consequently enstatite is also condensable as Mg-silicate. Which of forsterite and enstatite condenses is to be determined by the nature of Gibbs free energy surface which depends on the abundance of the vapor composed of Mg, SiO and H₂O.

Generally when sequential condensation occurs, the actual condensation sequence may differ from that predicted by the chemical equilibrium theory in view of the supercooling effect. In order to investigate in detail, we have to deal with the nucleation on multicomponent systems involving chemical reactions in saturated vapors. However the above-mentioned condensation sequence of iron and Mg-silicate will not be altered essentially.

We have to point out here another problem which is important in investigating the condensation sequence. Namely, if Ca-Al-rich refractory mineral grains have already condensed and act as core nuclei, it is possible for iron and Mg-silicate to condense heterogeneously on these grains. This process has not been considered clearly in the past studies. The degree of supercooling in this process will be less compared with the homogeneous nucleation. In the heterogeneous nucleation, the interfacial tension between metallic iron and the core minerals and that between Mg-silicate and the core minerals essentially determine the degree of supercooling of each condensate. These interfacial tensions are not known well. However if the interfacial tension between metallic iron and the core minerals are larger enough than that between Mg-silicate and the core minerals, which is probable considering the atomic structure of each material, we may expect that the condensation of Mg-silicate on the core grains will precede the condensation of metallic iron.

References

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