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Kinetic theory of steady chemical nucleation in the gas phase

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Abstract. We develop a kinetic theory of nucleation involving chemical reactions in the gas phase. For the basis of deriving the chemical nucleation rate, chemical kinetic considerations are presented on the steady current density and the effective rate constants of the overall reaction, which is a sum of a sequential elementary reactions. We formulate the steady rate of chemical nucleation in a multi-component vapor, in which nucleation occurs via the chemical reactions yielding a condensate having a stoichiometric composition. An exact expression of the steady nucleation rate is given together with its approximate formulas for practical applications. The present formulation is not concerned with any particular cluster model. The supersaturation ratio for a many-component vapor is defined so as to be a natural extension of that for a one-component vapor. It is shown that the transition probabilities due to growth and decay of the clusters are of the same form as the growth and evaporation rates in a one-component vapor.

Key words. astrochemistry – molecular processes – methods: analytical

1. Introduction

Nucleation is one of the important elementary processes of dust formation in astrophysical environments (see e.g., Sedlmayr & Dominik 1995) as well as of many phenomena studied in various fields of science and engineering. The study of the nucleation theory has concentrated mainly on nucleation in one-component systems, in which vapor and condensate are of the same composition such as in condensation of H_2O vapor into the liquid droplets. However, it is usual in many condensation phenomena that the composition of condensate is different from that of the vapor as are the cases of silicate and carbon dust formation in circumstellar space and many of the condensation experiments in laboratories (e.g., Nuth et al. 2000 and references therein). There are two cases where the vapor and the condensate are of different compositions: one is the case where the condensate is a mixture such as sulfuric acid–water mixtures in polluted air (see Hirschfelder 1974 and references therein). The other is the case where the condensate is formed through chemical reactions yielding a stoichiometric compound. The theory of nucleation of mixtures was formulated by Rice (1950) for binary systems, and was extended by Hirschfelder (1974) to many-component systems. On the other hand, the theory of chemical nucleation has not been well established.

In the astrophysical context, Gail & Sedlmayr (1988) made an attempt to formulate chemical nucleation, and proposed a method of calculating numerically the steady nucleation rate involving chemical reactions. The method requires the data of rate constants of the reactions involving clusters of various sizes, but most of the data are unavailable for the materials of interest. The analytic expression of the nucleation rate applicable when one growth species dominates like C_2H_2 in carbon dust formation in C-rich AGB stars is essentially equivalent to that for a one-component vapor. Kozasa & Hasegawa (1987) proposed a concept of a key species, which is the species of the least collision frequencies among the reactants relevant to the reactions accompanied with chemical nucleation. They assumed that the nucleation rate was controlled by two-body collisions between the clusters and the molecules of a key species. Chigai et al. (1999) derived a chemical nucleation rate employing the key–species concept. However, the validity of the key–species concept has not been examined.

Girshick (1997) obtained an exact expression of the nucleation rate in view of the nucleation in silane plasmas under conditions typical of amorphous silicon thin film deposition during the fabrication of integrated circuits. The reactions that he supposed are:

$$\mathrm{SiH_3^-} + \mathrm{SiH_4} \rightarrow \mathrm{Si_2H_5^-} + \mathrm{H_2},$$

$$\mathrm{Si_2H_5^-} + \mathrm{SiH_4} \rightarrow \mathrm{Si_3H_7^-} + \mathrm{H_2},$$

$$\ldots$$

$$\mathrm{Si}_{n-1}\mathrm{H}_{2n-1}^- + \mathrm{SiH_4} \rightarrow \mathrm{Si}_n\mathrm{H}_{2n+1}^- + \mathrm{H_2},$$

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which are expressed in general by

$$\mathrm{A}_i\mathrm{B}_{m+(i-1)(n-p)} + \mathrm{AB}_n \rightarrow \mathrm{A}_{i+1}\mathrm{B}_{m+i(n-p)} + \mathrm{B}_p \quad (i \geq 1). \tag{1}$$

The characteristics of this type of reactions are that these are equimolar reactions with only one kind of growth species AB_n, and that there is a starting block AB_m, which is regarded to be a monomer.

In astrophysical nucleation usually met, however, there is no starting block, and growth species more than one species participate in the reactions like, for example, TiC formation around C-stars (Chigai et al. 1999) through the reactions such that

$$\mathrm{Ti} + \mathrm{Ti} + \mathrm{C_2H_2} \rightarrow (\mathrm{TiC})_2 + \mathrm{H_2},$$

$$(\mathrm{TiC})_i + \mathrm{Ti} + \frac{1}{2}\mathrm{C_2H_2} \rightarrow (\mathrm{TiC})_{i+1} + \frac{1}{2}\mathrm{H_2} \quad (i \geq 2).$$

In this paper, we derive a steady nucleation rate applicable to nucleation involving more general types of chemical reactions than that Girshick (1997) supposed. The nucleation rate that we have obtained is an exact one free from any particular cluster model for the evaluation of the Gibbs free energy of formation of the clusters, and includes no "tuning parameter". Formulation is given for nucleation in ideal gases, but the results will be applicable to nucleation in ideal solutions as well if the rate constants are appropriately taken. Section 2 presents chemical kinetic considerations relevant to the formulation of the nucleation rate. The chemical nucleation rate and its approximate but concise expression are given in Sect. 3 and 5, respectively. The case when monomers are present is discussed in Sect. 4. Section 6 examines the validity of the key–species concept and clarifies a criterion of its applicability. Concluding remarks are presented in Sect. 7.

2. Chemical kinetic considerations

We present a chemical kinetic discussion on the current densities (which we call simply currents hereafter) and the rate constants of chemical reactions relevant to the formulation of the steady chemical nucleation rate given in Sect. 3. Chemical kinetics is applicable if elastic collisions dominate over reactive collisions in the Boltzmann equation, in other words, if the relaxation time of the velocity distribution function of gaseous molecules is much shorter than the time scale of the change in the gaseous composition through the chemical reactions (e.g., Kitahara 1994).

2.1. Elementary and overall reactions and their currents

It is essential in the following discussion to distinguish an *elementary reaction* and an *overall reaction.* The elementary reaction is an actual reaction that is a step of a series of successive reactions (e.g., McQuarrie & Simon 1997). In an elementary reaction, the products are formed directly from the reactants without passing intermediate compounds, thus the current of an elementary reaction is proportional to the product of the concentrations of the reactants (e.g., McQuarrie & Simon 1997). This is a basic postulate of chemical kinetics, implying that the rate constant of an elementary reaction is independent of the concentrations.

In consequence, the net current of the reaction

$$\mathcal{X} + \mathcal{B}_1 + \cdots + \mathcal{B}_n \rightleftharpoons \mathcal{Y} + \mathcal{D}_1 + \cdots + \mathcal{D}_m \tag{2}$$

is expressed by

$$J = kXB_1 \cdots B_n - \alpha Y D_1 \cdots D_m \tag{3}$$

if the forward and reverse reactions are elementary reactions. Here, X, B_i, Y, D_i represent the concentrations (which mean the number densities hereafter) of the molecular species $\mathcal{X}$, $\mathcal{B}_i$, $\mathcal{Y}$, and $\mathcal{D}_i$, and k and α are the rate constants, which are independent of the concentrations.

An overall reaction is a net reaction summed over successive elementary reactions given, for example, by

$$\mathcal{X} + \mathcal{B}_1 \rightleftharpoons \mathcal{Z}_1 + \mathcal{D}_{11} + \cdots, \tag{4}$$

$$\mathcal{Z}_1 + \mathcal{B}_2 \rightleftharpoons \mathcal{Z}_2 + \mathcal{D}_{21} + \cdots, \tag{5}$$

$$\cdots$$

$$\mathcal{Z}_{n-1} + \mathcal{B}_n \rightleftharpoons \mathcal{Y} + \mathcal{D}_{n1} + \cdots \tag{6}$$

The overall reaction of a sequence of these elementary reactions is expressed by

$$\mathcal{X} + \mathcal{B}_1 + \cdots + \mathcal{B}_n \rightleftharpoons \mathcal{Y} + \mathcal{F}_1 + \cdots, \tag{7}$$

where $\mathcal{F}_1 + \cdots = \mathcal{D}_{11} + \cdots + \mathcal{D}_{n1} + \cdots$. Here we have put the stoichiometric coefficients of the species participating in the reactions to be unity without loss of generality. It should be pointed out that one should distinguish the overall reaction (7) from the elementary reaction (2) despite their apparent identity; the reaction (7) is not a reaction that occurs as an elementary process, but is a sum of the set of the elementary reactions (4) to (6).

In the steady state, the net currents are all identical for those reactions including the overall reaction (7). We present a principle relation on the steady current for the overall reaction (7) expressed by

$$J = k_{\mathcal{X}} XB_1 \cdots B_n - \alpha_{\mathcal{Y}} Y F_1 \cdots, \tag{8}$$

where $k_{\mathcal{X}}$ and $\alpha_{\mathcal{Y}}$ are *not* independent of the concentrations but functions of the concentrations B_1, $\cdots$, B_n and F_1, $\cdots$, respectively. This is verified as follows: in the reaction (7), the forward current must vanish if any one of the concentrations of the molecular species $\mathcal{X}$, $\mathcal{B}_1$, $\cdots$, $\mathcal{B}_n$ participating in the forward reaction is zero, because all of them are required for the forward reaction to proceed. The forward current must thus include a factor $XB_1 \cdots B_n$. The same holds for the reverse current as well. In consequence, we have Eq. (8). The rate constants $k_{\mathcal{X}}$ and $\alpha_{\mathcal{Y}}$

are functions of the concentrations and remain finite in the tenuous limit where the concentrations tend to be zero.

The relation (8) states that the current of the overall reaction is of the same form as that of an elementary reaction but the rate constants are no longer independent of the concentrations. We call $k_{\mathcal{X}}$ and $\alpha_{\mathcal{Y}}$ that appear in the overall reaction the *effective rate constants* to distinguish from the rate constants in the elementary reactions. The effective rate constants depend on the rate constants of the elementary reactions as well as the concentrations of the molecular species $B_1, \cdots, B_n, F_1, \cdots$ participating in the overall reaction (7). It can be shown (see Appendix A) that the *ratio* of the effective rate constants $\alpha_{\mathcal{Y}}$ and $k_{\mathcal{X}}$ appearing in Eq. (8) is independent of the concentrations $B_1, \cdots, B_n$ and $F_1, \cdots$ in the overall reaction (7). This fact plays a basic role in deriving the steady nucleation rate as discussed in Sect. 3.

2.2. Multiple paths

In producing $\mathcal{Y}$ from $\mathcal{X}$ through successive reactions with $\mathcal{B}_1, \cdots, \mathcal{B}_n$, there are $n!$ paths depending on the order of the reactions with $\mathcal{B}_1, \cdots, \mathcal{B}_n$ if $\mathcal{B}_1, \cdots, \mathcal{B}_n$ are different species with each other. The total current is given by the sum of the current J_i given by the form (8) for each path i:

$$J = kXB_1 \cdots B_n - \alpha Y F_1 \cdots \tag{9}$$

with

$$k = \sum_i k_i, \quad \alpha = \sum_i \alpha_i = \sum_i \beta_i k_i, \tag{10}$$

where the summation is taken over $n!$ paths, and $\beta_i \equiv \alpha_i / k_i$ is concentration-independent. Note that the "rate constants" of the total reaction are given by the sum of the effective rate constants for each path. The paths having the largest k_i and α_i contribute most to the total current J.

In what follows, we discuss the current for one path for each successive reaction and omit the suffix i from J_i.

3. Formulation of the chemical nucleation rate

3.1. Definition of the equilibrium state

We define an equilibrium state to be a state in which a vapor and a *bulk* condensate coexist in a closed system at a given temperature and pressure. The vapor consists of molecules and clusters of various sizes from which grains will form. The present definition of equilibrium is the same as that employed by Patzer et al. (1998) following Katz & Wiedersich (1977), and does not mean a metastable supersaturated–state in the absence of a bulk condensate employed in the conventional nucleation theory (e.g., Feder et al. 1966; Abraham 1974).

The equilibrium state has the following important properties: 1) Both vapor and bulk condensate are of equal temperature, 2) the forward current equals the reverse current for any reaction of both elementary and overall reactions, thus $J = 0$ for any reaction, and 3) chemical equilibrium is realized among various species and phases, implying that the sums of chemical potentials of the reactants and of the products are equal for any reaction involving various molecular species in the vapor and bulk condensate.

The equilibrium state is used as a reference state in dealing with actual states usually in a supersaturated state, in which nucleation occurs. The quantities in the equilibrium state are denoted by putting dot "$\cdot$" above their symbols hereafter, which we use instead of "$\circ$" used, for example, by Patzer et al. (1998) to avoid confusion with quantities at a standard pressure. The readers should not misunderstand that the dot indicates time derivative.

3.2. Steady nucleation rate

We shall deal with steady nucleation involving chemical reactions in which n kinds of reactants $\mathcal{B}_1, \cdots, \mathcal{B}_n$ participate in the reaction. Furthermore, we do not assume in general the presence of monomers having the same composition as the grains and clusters whose size is larger than a certain size. The clusters with sizes larger than a certain size, for which we put p, will have the same composition as the grains of a macroscopic size, say, larger than $0.1\,\mu$m. We do not consider cluster–cluster reactions (Patzer et al. 1998) but deal with stepwise growth and dissociation of the clusters $\mathcal{A}_i$, i.e. $\mathcal{A}_i \rightleftharpoons \mathcal{A}_{i+1}$. The stepwise growth is realized if the concentrations of the reactants are large compared with those of the clusters. Furthermore, we restrict our discussion to the case that reactant molecules and clusters of various sizes are of equal temperature, i.e. in the LTE state in the sense of Patzer et al. (1998).

In the situation stated above, the clusters of size i ($>p$) grow to the size $i+1$ through the reactions with $\mathcal{B}_1, \cdots, \mathcal{B}_n$. For $i \geq p$, the overall reaction for the formation of a cluster $\mathcal{A}_{i+1}$ from a cluster $\mathcal{A}_i$ is written as

$$\mathcal{A}_i + \mathcal{B}_1 + \cdots + \mathcal{B}_n \rightleftharpoons \mathcal{A}_{i+1} + \sum_k f_k \mathcal{F}_k \qquad (i \geq p), \tag{11}$$

where $\mathcal{F}_k$ are the product species other than $i+1$-mers, $\mathcal{A}_{i+1}$, and f_k are the stoichiometric coefficients. The elementary reactions to reach p-mers, $\mathcal{A}_p$, cannot be specified in general, but the overall reaction is written as

$$p(\mathcal{B}_1 + \cdots + \mathcal{B}_n) \rightleftharpoons \mathcal{A}_p + p \sum_k f_k \mathcal{F}_k. \tag{12}$$

Here we have assumed that the reactants for the $\mathcal{A}_p$ formation are the same as those for $\mathcal{A}_i$ ($i \geq p$) formation. The net reaction for forming $\mathcal{A}_i$ from the reactant $\mathcal{B}_1, \cdots, \mathcal{B}_n$ is given by

$$i(\mathcal{B}_1 + \cdots + \mathcal{B}_n) \rightleftharpoons \mathcal{A}_i + i \sum_k f_k \mathcal{F}_k. \tag{13}$$

In the bulk limit of $i \to \infty$, the reaction (13) is expressed by

$$\mathcal{B}_1 + \cdots + \mathcal{B}_n \rightleftharpoons \mathcal{A}_{\mathrm{s}} + \sum_k f_k \mathcal{F}_k, \tag{14}$$

where $\mathcal{A}_\mathrm{s}$ represents a molecular unit of the bulk condensate.

Let us denote the concentrations (i.e. number densities) of $\mathcal{B}_1, \cdots, \mathcal{B}_n$ by $c_1, \cdots, c_n$, respectively, those of $\mathcal{F}_k$ by $c_{\mathcal{F}_k}$, and those of $\mathcal{A}_i$ by $c(i)$. From Eq. (8), the steady current, which equals the steady nucleation rate here, is expressed by

$$J = k_i c_1 \cdots c_n c(i) - \alpha_{i+1} \prod_k c_{\mathcal{F}_k}^{f_k} \cdot c(i+1) \tag{15}$$

for the reaction (11), where k_i and α_{i+1} are the effective forward and reverse rate constants, respectively. For the reaction (12), the steady nucleation rate is expressed by

$$J = k_{1,p}(c_1 \cdots c_n)^p - \alpha_p \prod_k \left(c_{\mathcal{F}_k}^{f_k}\right)^p \cdot c(p), \tag{16}$$

where $k_{1,p}$ and α_p are the effective rate constants. Note that both J given by Eqs. (15) and (16) are equal in the steady state.

Since $J = 0$ in equilibrium, we can rewrite J given by (16) and (15) with the use of the equilibrium concentrations as

$$\begin{aligned} J &= k_{1,p}(c_1 \cdots c_n)^p \left[1 - \frac{1}{S^p} \cdot \frac{c(p)}{\dot{c}(p)}\right] & (17) \\ &= k_i c_1 \cdots c_n \dot{c}(i) \left[\frac{c(i)}{\dot{c}(i)} - \frac{1}{S} \cdot \frac{c(i+1)}{\dot{c}(i+1)}\right] \quad (i \geq p), & (18) \end{aligned}$$

where $\dot{c}(i)$, etc. are the equilibrium concentrations, and S is defined by

$$S = \frac{c_1 \cdots c_n}{\dot{c}_1 \cdots \dot{c}_n} \prod_k \left(\frac{\dot{c}_{\mathcal{F}_k}}{c_{\mathcal{F}_k}}\right)^{f_k} = \frac{P_1 \cdots P_n}{\dot{P}_1 \cdots \dot{P}_n} \prod_k \left(\frac{\dot{P}_{\mathcal{F}_k}}{P_{\mathcal{F}_k}}\right)^{f_k}, \tag{19}$$

where $P_i = c_i k_\mathrm{B} T$ and $\dot{P}_i = \dot{c}_i k_\mathrm{B} T$ with k_B being Boltzmann's constant. In deriving Eqs. (17) and (18), we have used the relations $\alpha_p / k_{1,p} = \dot{\alpha}_p / \dot{k}_{1,p}$ and $\alpha_{i+1}/k_i = \dot{\alpha}_{i+1}/\dot{k}_i$ (see Sect. 2.1), where $\dot{k}_i$, $\dot{\alpha}_{i+1}$, etc. are the effective rate constants for the equilibrium concentrations. From the recurrence relations (17) and (18), J is obtained by the conventional procedure (e.g., Katz & Wiedersich 1977; Kozasa & Hasegawa 1987; Gail & Sedlmayr 1988; Patzer et al. 1998; Chigai et al. 1999). Namely, multiplying $1/S^i$ on both sides of Eq. (18) divided by $k_i c_1 \cdots c_n \dot{c}(i)$ successively for $i = p, p+1, p+2, \cdots$, summing over i, and adding Eq. (17) divided by $k_{1,p}(c_1 \cdots c_n)^p$, we obtain

$$\frac{1}{J} = \frac{1}{c_1 \cdots c_n} \left[\frac{1}{k_{1,p}(c_1 \cdots c_n)^{p-1}} + \sum_{i=p}^{\infty} \frac{1}{k_i S^i \dot{c}(i)}\right], \tag{20}$$

where we have used

$$\lim_{i \to \infty} \frac{1}{S^{i+1}} \cdot \frac{c(i+1)}{\dot{c}(i+1)} = 0 \tag{21}$$

for $S > 1$. The proof of Eq. (21) is given in Appendix B.

From the equilibrium condition of the reaction (13) of i-mer formation, we have

$$i \sum_{j=1}^{n} \dot{\mu}_j = \dot{\mu}(i) + i \sum_k f_k \dot{\mu}_{\mathcal{F}_k}, \tag{22}$$

where the chemical potentials per molecule of $\mathcal{B}_j$ in equilibrium are denoted by $\dot{\mu}_j$, those of $\mathcal{A}_i$ by $\dot{\mu}(i)$, and those of $\mathcal{F}_k$ by $\dot{\mu}_{\mathcal{F}_k}$. For a gaseous species a of partial pressure $\dot{P}_a$ and temperature T, the chemical potential per molecule is expressed (e.g., Landau & Lifschitz 1980) by

$$\dot{\mu}_a = \chi_a + k_\mathrm{B} T \ln \frac{\dot{P}_a}{P_0} = \chi_a + k_\mathrm{B} T \ln \frac{\dot{c}_a k_\mathrm{B} T}{P_0}$$

if the vapor can be regarded to be an ideal gas, where χ_a is the chemical potential per molecule at a standard pressure P_0. Using this expression for the chemical potentials in Eq. (22), we obtain the equilibrium concentrations $\dot{c}(i)$ of $\mathcal{A}_i$ as

$$\begin{aligned} \dot{c}(i) &= \frac{P_0}{k_\mathrm{B} T} \mathrm{e}^{-g^\circ(i)} \left[\frac{\dot{P}_1 \cdots \dot{P}_n}{P_0^n} \prod_k \left(\frac{P_0}{\dot{P}_{\mathcal{F}_k}}\right)^{f_k}\right]^i \\ &= \frac{P_0}{k_\mathrm{B} T} \mathrm{e}^{-g^\circ(i)} \frac{1}{S^i} \left[\frac{P_1 \cdots P_n}{P_0^n} \prod_k \left(\frac{P_0}{P_{\mathcal{F}_k}}\right)^{f_k}\right]^i \end{aligned} \tag{23}$$

with

$$g^\circ(i) = \frac{1}{k_\mathrm{B} T} \left[\chi(i) + i \sum_k f_k \chi_{\mathcal{F}_k} - i \sum_{j=1}^{n} \chi_j\right] \quad (i \geq p). \tag{24}$$

Substitution of $\dot{c}(i)$ given by Eq. (23) into Eq. (20) leads to the steady nucleation rate J expressed in terms of the given quantities as

$$\begin{aligned} \frac{1}{J} = \frac{1}{c_1 \cdots c_n} \Bigg[& \frac{1}{k_{1,p}(c_1 \cdots c_n)^{p-1}} \\ & + \sum_{i=p}^{\infty} \left\{ k_i \frac{P_0}{k_\mathrm{B} T} \left[\frac{P_1 \cdots P_n}{P_0^n} \prod_k \left(\frac{P_0}{P_{\mathcal{F}_k}}\right)^{f_k}\right]^i \mathrm{e}^{-g^\circ(i)} \right\}^{-1} \Bigg]. \end{aligned} \tag{25}$$

3.3. One-component system

To examine the steady chemical nucleation rate given by Eq. (25), let us discuss the simplest case, i.e. a one-component system in this subsection. The reaction for i-mer formation is given by

$$\mathcal{A}_i + \mathcal{A} \rightleftharpoons \mathcal{A}_{i+1} \quad (i \geq 1). \tag{26}$$

Comparing this reaction with the reaction (11), we see $n = p = 1$, $f_k = 0$, $c_1 = c(1)$ and $\mathcal{B}_1 = \mathcal{A}$, indicating that the reactant $\mathcal{B}_1$ acts as a monomer $\mathcal{A}$ in this case; the reaction (12) reduces to an identical reaction, and needs not to be taken into account. In addition, S defined by Eq. (19) reduces to

$$S = P_1/\dot{P}_1, \tag{27}$$

which equals a supersaturation ratio in a one-component system. For a one-component system, the rate constant is expressed by $k_i = \langle \sigma_i v \rangle$ with using cross section σ_i of an i-mer for collisional sticking of monomers, and velocity v of monomers relative to the i-mer, where $\langle \cdots \rangle$ indicates an average over a Maxwellian velocity distribution. For ideal gases, k_i is given by $k_i = \alpha s_i \sqrt{k_\mathrm{B} T/2\pi m}$, where α is the condensation coefficient, s_i is the surface area of an i-mer, and m is the reduced mass of a monomer and an i-mer, almost equal to a monomer mass if $i \gg 1$. It is easily confirmed that, for α being independent of the monomer concentration, Eq. (20) for $n = 1$ reduces to Eq. (9) of Katz & Wiedersich (1977), who derived the steady nucleation rate for a one-component system by defining the equilibrium state to be a saturated state as stated in Sect. 3.1.

Ignoring the first term on the RHS of Eq. (25) resulting from the reaction (12), we have

$$\begin{aligned}\frac{1}{J} &= \sum_{i=1}^{\infty}\left\{k_i c_1 \frac{P_0}{k_\mathrm{B}T}\frac{P_1}{P_0}\left(\frac{P_1}{P_0}\right)^{i-1} \mathrm{e}^{-g^\circ(i)}\right\}^{-1} \\ &= \sum_{i=1}^{\infty}\left\{k_i c_1^2 \mathrm{e}^{-g(i)}\right\}^{-1} \end{aligned}\tag{28}$$

with

$$g^\circ(i) = [\chi(i) - i\chi_1]/k_\mathrm{B}T, \tag{29}$$

$$g(i) = [\chi(i) - i\chi_1]/k_\mathrm{B}T - (i-1)\ln(P_1/P_0). \tag{30}$$

From a comparison of Eq. (28) with the conventional nucleation rate for a one-component system (e.g., Feder et al. 1966; Abraham 1974), we see that $k_\mathrm{B}Tg(i)$ is the minimum work needed to form an i-mer $\mathcal{A}_i$ from monomers $\mathcal{A}$ (Landau & Lifschitz 1980); the minimum work equals the Gibbs free energy change for formation of $\mathcal{A}_i$ from $\mathcal{A}$ if the clusters and the vapor in a closed system are of equal temperature and pressure (Landau & Lifschitz 1980).

To obtain a more familiar expression of $g(i)$, let us introduce the equilibrium state as a reference state, and consider chemical equilibrium between monomers and a bulk condensate (cf. Eq. (14)):

$$\mathcal{A} \rightleftharpoons \mathcal{A}_\mathrm{s}. \tag{31}$$

The equilibrium condition of this reaction, $\dot{\mu}_1 = \mu_\mathrm{s}$, is expressed by

$$\chi_1 + k_\mathrm{B}T \ln\frac{\dot{P}_1}{P_0} = \mu_\mathrm{s} \tag{32}$$

where μ_s is the chemical potential per $\mathcal{A}_\mathrm{s}$, and is independent of pressures concerned. From Eqs. (27) and (32), the supersaturation ratio S is expressed by

$$\ln S = \ln\frac{P_1}{P_0} - \frac{\mu_\mathrm{s} - \chi_1}{k_\mathrm{B}T} = \frac{\mu_1 - \mu_\mathrm{s}}{k_\mathrm{B}T}, \tag{33}$$

where μ_1 is the chemical potential of a monomer $\mathcal{A}$ defined for a supersaturated (i.e. nonequilibrium) state (e.g., Kitahara 1994), and is given by

$$\mu_1 = \chi_1 + k_\mathrm{B}T\ln(P_1/P_0). \tag{34}$$

As is expected, $\ln S = 0$ in equilibrium from Eq. (32).

Rewriting $g(i)$ given by Eq. (30) with the use of μ_s and Eq. (33), we obtain

$$\begin{aligned} g(i) &= -(i-1)\left(\ln\frac{P_1}{P_0} - \frac{\mu_\mathrm{s} - \chi_1}{k_\mathrm{B}T}\right) \\ &\quad + \frac{\chi(i) - \chi_1 - (i-1)\mu_\mathrm{s}}{k_\mathrm{B}T} \end{aligned}\tag{35}$$

$$= -(i-1)\ln S + \frac{\chi(i) - \chi_1 - (i-1)\mu_\mathrm{s}}{k_\mathrm{B}T}\cdot \tag{36}$$

For $i \gg 1$, $g(i)$ is approximated to be:

$$g(i) \simeq -i\ln S + \frac{\chi(i) - i\mu_\mathrm{s}}{k_\mathrm{B}T}, \tag{37}$$

where the first and second terms represent the volume and the surface energies, respectively.

3.4. Another expression of the steady chemical nucleation rate

Rewriting Eq. (25) in the similar manner as in Eq. (28), we have

$$\begin{aligned}\frac{1}{J} &= \frac{1}{c_1\cdots c_n}\left[\frac{1}{k_{1,p}(c_1\cdots c_n)^{p-1}}\right. \\ &\quad \left. + \sum_{i=p}^{\infty}\left\{k_i \frac{P_0}{k_\mathrm{B}T}\frac{P_1\cdots P_n}{P_0^n}\prod_k\left(\frac{P_0}{P_{\mathcal{F}_k}}\right)^{f_k}\mathrm{e}^{-g(i)}\right\}^{-1}\right], \end{aligned}\tag{38}$$

where $g(i)$ is defined by

$$\begin{aligned} g(i) &= g^\circ(i) - (i-1)\ln\left[\frac{P_1\cdots P_n}{P_0^n}\prod_k\left(\frac{P_0}{P_{\mathcal{F}_k}}\right)^{f_k}\right] \\ &= \frac{1}{k_\mathrm{B}T}\left\{ -(i-1)\left[\sum_{j=1}^{n}\mu_j - \sum_k f_k\mu_{\mathcal{F}_k}\right]\right. \\ &\quad \left. + \left[\chi(i) + \sum_k f_k\chi_{\mathcal{F}_k} - \sum_{j=1}^{n}\chi_j\right]\right\}, \end{aligned}\tag{39}$$

where

$$\mu_a = \chi_a + k_\mathrm{B}T\ln\frac{P_a}{P_0} \qquad (a \text{ is } \mathcal{B}_j \text{ or } \mathcal{F}_k) \tag{40}$$

is the chemical potential per molecule of gaseous species a at partial pressure P_a (cf. Eq. (34)). Using the chemical potential μ_s per $\mathcal{A}_\mathrm{s}$ of the bulk condensate, $g(i)$ is expressed by

$$\begin{aligned} g(i) &= \frac{1}{k_\mathrm{B}T}\left[-(i-1)\left(\sum_{j=1}^{n}\mu_j - \mu_\mathrm{s} - \sum_k f_k\mu_{\mathcal{F}_k}\right)\right. \\ &\quad \left. + \left(\chi(i) - (i-1)\mu_\mathrm{s} + \sum_k f_k\chi_{\mathcal{F}_k} - \sum_{j=1}^{n}\chi_j\right)\right], \end{aligned}\tag{41}$$

which reduces to the minimum work $g(i)$ given by Eq. (35) when $n = 1$ and $f_k = 0$, implying that $g(i)$ represents the minimum work to form an i-mer $\mathcal{A}_i$ from reactant molecules $\mathcal{B}_1, \cdots, \mathcal{B}_n$ for $i \gg 1$.

3.5. Supersaturation ratio

The equilibrium condition of the reaction (14) is expressed by

$$\mu_{\rm s} + \sum_k f_k \dot{\mu}_{\mathcal{F}_k} - \sum_{j=1}^{n} \dot{\mu}_j = 0. \tag{42}$$

Subtracting the LHS of Eq. (42) divided by $k_{\rm B}T$ from $\ln S$ with S defined by Eq. (19), we have

$$\ln S = \frac{1}{k_{\rm B}T}\left(\sum_{j=1}^{n} \mu_j - \mu_{\rm s} - \sum_k f_k \mu_{\mathcal{F}_k}\right), \tag{43}$$

which reproduces the supersaturation ratio given by Eq. (33) for a one-component system by putting $n = 1$ and $f_k = 0$, so S given by Eq. (43) is regarded to be a natural extension of the supersaturation ratio to a many-component system (Kozasa & Hasegawa 1987).

In terms of the supersaturation ratio S newly defined by Eq. (43), $g(i)$ given by Eq. (41) is expressed as

$$g(i) = -(i-1)\ln S + \frac{1}{k_{\rm B}T}\left\{\chi(i) - (i-1)\mu_{\rm s} + \sum_k f_k \chi_{\mathcal{F}_k} - \sum_{j=1}^{n} \chi_j\right\}. \tag{44}$$

If $i \gg 1$, $g(i)$ may be approximated leading to the same form as given by Eq. (37) for the one-component system. The first term on the RHS represents the volume energy of an i-mer as is in the one-component system. The second term, which is proportional to $\chi(i) - i\mu_{\rm s}$ if $i \gg 1$, indicates the energy difference arising from the free surface, when an i-mer from the bulk condensate is moved into the vapor. Thus, $\chi(i) - i\mu_{\rm s} \propto i^{2/3}$ if $i \gg 1$ for spherical i-mers, and represents the surface energy. In consequence, $g(i)$ given by Eq. (44) is approximated if $i \gg 1$ to be:

$$g(i) \simeq -i \ln S + \theta_\infty i^{2/3} \tag{45}$$

with

$$\theta_\infty = \frac{4\pi\sigma a_0^2}{k_{\rm B}T}, \tag{46}$$

where σ is the surface tension of the bulk condensate, and a_0 is the equivalent radius of a molecular unit of the bulk condensate. It should be noted that $g(i)$ given by Eq. (44) attains a maximum at $i = i_*$ given by

$$i_* \simeq \left(\frac{2\theta_\infty}{3\ln S}\right)^3, \tag{47}$$

if $i_* \gg 1$.

3.6. Transition probabilities

The steady nucleation rate (15) is expressed as

$$J = p_i c(i) - r_{i+1} c(i+1) \tag{48}$$

with

$$p_i = k_i c_1 \cdots c_n \quad \text{and} \quad r_{i+1} = \alpha_{i+1} \prod_k c_{\mathcal{F}_k}^{f_k}. \tag{49}$$

In a one-component system, p_i is the growth rate, i.e. the number of monomers sticking onto an i-mer per unit time, and r_{i+1} is the evaporation rate, i.e. the number of monomers evaporating from $i+1$-mer per unit time. In an n-component system, p_i indicates the probability of transition from $\mathcal{A}_i$ to $\mathcal{A}_{i+1}$ per unit time, and r_{i+1} the probability of transition from $\mathcal{A}_{i+1}$ to $\mathcal{A}_i$ per unit time.

The ratio of the transition probabilities is given from Eq. (49) by

$$\frac{r_{i+1}}{p_i} = \frac{1}{S} \cdot \frac{\alpha_{i+1} \prod_k \dot{c}_{\mathcal{F}_k}^{f_k}}{k_i \dot{c}_1 \cdots \dot{c}_n} \tag{50}$$

with the use of Eq. (19). Since $J = 0$ in equilibrium, we have

$$\frac{\dot{r}_{i+1}}{\dot{p}_i} = \frac{\dot{\alpha}_{i+1} \prod_k \dot{c}_{\mathcal{F}_k}^{f_k}}{\dot{k}_i \dot{c}_1 \cdots \dot{c}_n} = \frac{\dot{c}(i)}{\dot{c}(i+1)} \tag{51}$$

from Eqs. (49) and (48). Equations (50) and (51) yield

$$\frac{r_{i+1}}{p_i} = \frac{1}{S} \cdot \frac{\dot{c}(i)}{\dot{c}(i+1)}, \tag{52}$$

where we have put $(\alpha_{i+1}/k_i)/(\dot{\alpha}_{i+1}/\dot{k}_i) = 1$ (see Sect. 2.1). The equilibrium concentrations $\dot{c}(i)$ and $\dot{c}(i+1)$ are given by Eq. (23), which leads with the use of Eq. (39) to

$$\frac{\dot{c}(i)}{\dot{c}(i+1)} = S \exp[g(i+1) - g(i)]. \tag{53}$$

Thus, the ratio of the transition probabilities (50) is given by

$$\frac{r_{i+1}}{p_i} = \exp[g(i+1) - g(i)]. \tag{54}$$

The relation (54) is of exactly the same form as the ratio of the evaporation rate to the growth rate for a one–component system, and indicates that $r_{i+1}/p_i > 1$ for cluster sizes i with $g'(i) > 0$ and $r_{i+1}/p_i < 1$ for sizes i with $g'(i) < 0$. The clusters for which the forward transition probability equals the reverse current are the critical clusters, whose size i_* is given by the size where $g(i)$ attains a maximum ($g'(i_*) = 0$), i.e. by a solution to

$$\chi'(i_*) = \mu_{\rm s} + k_{\rm B}T \ln S \tag{55}$$

from Eq. (44). These results confirm that $g(i)$ given by Eq. (44) has the properties required for the minimum work needed to form an i-mer of sizes $i \lesssim i_*$ as well as of $i \gg 1$ as discussed in Sect. 3.4.

4. Steady chemical nucleation rate in the presence of monomers

The reaction (1) that Girshick (1997) dealt with is expressed as

$$\mathcal{A}_i + \mathcal{B}_1 \rightarrow \mathcal{A}_{i+1} + \mathcal{F}_1 \quad (i \geq 1). \tag{56}$$

A characteristic of this reaction is the presence of monomers $\mathcal{A}_1$ from which a sequence of the reactions starts. Here we deal with an extended type of such reactions

$$\mathcal{A}_i + \mathcal{B}_1 + \cdots + \mathcal{B}_n \rightarrow \mathcal{A}_{i+1} + \sum_k f_k \mathcal{F}_k \quad (i \geq 1), \tag{57}$$

which is an overall reaction, and is comparable to a set of the reactions of (11) and (12) in the absence of monomers, where a monomer $\mathcal{A}_1$ nominally corresponds to

$$\mathcal{A}_1 \equiv \mathcal{B}_1 + \cdots + \mathcal{B}_n - \sum_k f_k \mathcal{F}_k \tag{58}$$

from Eq. (12) for $p = 1$. The net reaction for forming $\mathcal{A}_i$ from $\mathcal{A}_1$ and $\mathcal{B}_1$, $\cdots$, $\mathcal{B}_n$ is expressed by

$$\mathcal{A}_1 + (i-1)(\mathcal{B}_1 + \cdots + \mathcal{B}_n) \rightarrow \mathcal{A}_i + (i-1)\sum_k f_k \mathcal{F}_k \quad (i \geq 1), \tag{59}$$

which is comparable to the reaction (13).

The steady nucleation rate for the reaction (57) is given by

$$\begin{aligned} J &= k_i c(i) c_1 \cdots c_n - \alpha_{i+1} c(i+1) \prod_k c_{\mathcal{F}_k}^{f_k} \\ &= k_i \dot{c}(i) c_1 \cdots c_n \left[\frac{c(i)}{\dot{c}(i)} - \frac{1}{S} \cdot \frac{c(i+1)}{\dot{c}(i+1)} \right], \end{aligned} \tag{60}$$

which holds for $i \geq 1$ because of the presence of monomers. Similar calculations as in Sect. 3 yield

$$\begin{aligned} \frac{1}{J} &= \frac{1}{c(1) c_1 \cdots c_n} \\ &\times \sum_{i=1}^{\infty} \left\{ k_i \left[\frac{P_1 \cdots P_n}{P_0^n} \prod_k \left(\frac{P_0}{P_{\mathcal{F}_k}} \right)^{f_k} \right]^{i-1} \mathrm{e}^{-g^\circ(i)} \right\}^{-1}, \end{aligned} \tag{61}$$

where

$$\begin{aligned} g^\circ(i) = \frac{1}{k_{\mathrm{B}} T} \Bigg[& \chi(i) + (i-1) \sum_k f_k \chi_{\mathcal{F}_k} - \chi(1) \\ & -(i-1) \sum_{j=1}^{n} \chi_j \Bigg]. \end{aligned} \tag{62}$$

Note that $g^\circ(i)$ given by Eq. (62) is the same as that defined by Eq. (24) in the absence of monomers if one makes a formal identification given by Eq. (66) below. In terms of the minimum work for i-mer formation given by

$$\begin{aligned} g(i) &= g^\circ(i) - (i-1) \ln \left[\frac{P_1 \cdots P_n}{P_0^n} \prod_k \left(\frac{P_0}{P_{\mathcal{F}_k}} \right)^{f_k} \right] \\ &= -(i-1) \ln S + \{ \chi(i) - \chi(1) - (i-1) \mu_{\mathrm{s}} \} / k_{\mathrm{B}} T \end{aligned} \tag{63}$$

with S given by Eq. (43), the steady nucleation rate J is expressed by

$$\frac{1}{J} = \frac{1}{c(1) c_1 \cdots c_n} \sum_{i=1}^{\infty} \left\{ k_i \mathrm{e}^{-g(i)} \right\}^{-1}, \tag{64}$$

which is comparable to Eq. (38).

It is worth pointing out that the nucleation rate (64) can also be derived from Eq. (38) by the following purely formal procedure, which may help understanding the difference between the reaction (57) and a set of the reactions (11) and (12) with putting $p = 1$ formally. Writing the reaction (13) as

$$\begin{aligned} & \underbrace{\left[\mathcal{B}_1 + \cdots + \mathcal{B}_n - \sum_k f_k \mathcal{F}_k \right]}_{\mathcal{A}_1} + (i-1)(\mathcal{B}_1 + \cdots + \mathcal{B}_n) \\ & \rightarrow \mathcal{A}_i + (i-1) \sum_k f_k \mathcal{F}_k, \end{aligned}$$

and identifying a monomer $\mathcal{A}_1$ to that given by Eq. (58), then one can put formally

$$\mu(1) \equiv \mu_1 + \cdots + \mu_n - \sum_k f_k \mu_{\mathcal{F}_k} \tag{65}$$

$$\chi(1) \equiv \chi_1 + \cdots + \chi_n - \sum_k f_k \chi_{\mathcal{F}_k}. \tag{66}$$

Applying the relation $\mu - \chi = k_{\mathrm{B}} T \ln(P/P_0)$ for an ideal gas formally, one obtains

$$\frac{P_0}{k_{\mathrm{B}} T} \frac{P_1 \cdots P_n}{P_0^n} \prod_k \left(\frac{P_0}{P_{\mathcal{F}_k}} \right)^{f_k} = c(1) \tag{67}$$

by taking difference of both sides of Eqs. (65) and (66). The minimum work $g(i)$ given by Eq. (41) turns out to be Eq. (63) because of Eq. (66), thus the nucleation rate given by Eq. (38) without the first term of the r.h.s to be Eq. (64) from Eq. (67).

It is easily confirmed that the nucleation rate given by Eq. (61) reduces to that for a one-component system given by Eq. (28) by putting $n = 1$, $f_k = 0$ for all k and $c(1) = c_1$.

Girshick's reaction (56) corresponds to the case

$$n = 1, \quad f_1 = 1, \quad f_k = 0 \quad (k \geq 2)$$

in the reaction (57). In this case, Eq. (61) with Eq. (62) reduces to

$$\frac{1}{J} = \frac{1}{c(1) c_1} \sum_{i=1}^{\infty} \left\{ k_i \left(\frac{P_1}{P_{\mathcal{F}_1}} \right)^{i-1} \mathrm{e}^{-g^\circ(i)} \right\}^{-1} \tag{68}$$

with

$$g^\circ(i) = \frac{1}{k_{\mathrm{B}} T} \left[\chi(i) + (i-1) \chi_{\mathcal{F}_1} - \chi(1) - (i-1) \chi_1 \right], \tag{69}$$

which reproduces Eq. (18) for $M \rightarrow \infty$ in Girshick (1997).

5. Approximate formula of the chemical nucleation rate

In the evaluation of the nucleation rate J given by Eq. (38), we consider a situation that the formation of p-mer is so fast that the first term in the r.h.s of Eq. (38), which term is relevant to the p-mer formation, can be ignored. If it is not the case, a bottleneck of condensation of grains occurs before the clusters grow to p-mers, and the molecular processes of the p-mer formation become a problem to discuss, which is not a purpose of this paper.

In the situation stated above, we derive an approximate expression of the nucleation rate J. Replacing the summation in J given by Eq. (38) by an integral, we have

$$\sum_{i=p}^{\infty} \left\{ k_i \mathrm{e}^{-g(i)} \right\}^{-1} \simeq \int_p^{\infty} \mathrm{d}i \, \frac{\mathrm{e}^{g(i)}}{k_i} \cdot$$

When the minimum work $g(i)$ given by Eq. (44) has a maximum at $i = i_*$, a rate-determining step of nucleation is growth of the clusters with sizes around $i = i_*$. If $i_* \gg p$ and k_i is a slowly varying function of i, the integral can be evaluated by the saddle point method with expanding $g(i)$ around $i = i_*$ as

$$g(i) \simeq g(i_*) + \frac{g''(i_*)}{2}(i - i_*)^2$$

and extending the lower limit of the integral to $-\infty$. The result is given by

$$\sum_{i=p}^{\infty} \left\{ k_i \mathrm{e}^{-g(i)} \right\}^{-1} \simeq \frac{\mathrm{e}^{g(i_*)}}{Z k_{i*}},$$

where $Z = \sqrt{-g''(i_*)/2\pi}$ is the Zeldovich factor, which is a correction factor if the summation is represented by the maximum term at $i = i_*$. Thus, the nucleation rate J given by Eq. (38) is approximated to be:

$$J \simeq Z k_{i_*} c_1 \cdots c_n \frac{P_0}{k_{\mathrm{B}} T} \frac{P_1 \cdots P_n}{P_0^n} \prod_k \left(\frac{P_0}{P_{\mathcal{F}_k}} \right)^{f_k} \mathrm{e}^{-g(i_*)}, \quad (70)$$

which is a good approximation if $-g''(i_*) \gg 1$. The size i_* of a critical nucleus is given by a solution of Eq. (55), and is approximated by Eq. (47) if $i_* \gg 1$, while the Zeldovich factor is expressed by

$$Z = \sqrt{\frac{-\chi''(i_*)}{2\pi k_{\mathrm{B}} T}} \quad (71)$$

from Eq. (44).

6. Key species

In dealing with nucleation accompanied with chemical reactions, Kozasa & Hasegawa (1987) assumed that the nucleation rate was controlled by two-body collisions between the clusters and the molecules of a key species, which was defined as the species of the least collision frequencies among the reactants. Employing the key species concept, Chigai et al. (1999) have shown that the rate of steady chemical nucleation is expressed by a factor Π times the steady nucleation rate for a one-component vapor ignoring the species other than the key species, where Π is a function of partial pressures of the reactants and gaseous products other than the key species. If we denote the key species by $\mathcal{B}_1$, the nucleation rate of Chigai et al. (1999) is expressed by

$$J = Z \Pi c_1^2 \langle \sigma_{i_*} v \rangle \mathrm{e}^{-g(i_*)}, \quad (72)$$

where

$$\Pi = \frac{P_2 \cdots P_n}{{P_0}^{n-1}} \prod_k \left(\frac{P_0}{P_{\mathcal{F}_k}} \right)^{f_k}, \quad (73)$$

and $\langle \sigma_{i_*} v \rangle$ is the rate constant for the reaction between a critical nucleus and a molecule of the key species, which is expressed by the product of the reaction cross section σ_{i_*} of the critical nucleus and their relative velocity v averaged over a Maxwellian velocity distribution.

Separating the quantities concerning $\mathcal{B}_1$, we can express the nucleation rate given by Eq. (38) as

$$\begin{aligned} \frac{1}{J} &= \frac{1}{k_{1,p}(c_1 \cdots c_n)^p} + \frac{1}{\Pi c_1^2} \sum_{i=p}^{\infty} \left\{ k'_i \mathrm{e}^{-g(i)} \right\}^{-1} \\ &\simeq \left(Z \Pi c_1^2 k'_{i_*} \mathrm{e}^{-g(i_*)} \right)^{-1}, \end{aligned} \quad (74)$$

where

$$k'_i = k_i c_2 \cdots c_n. \quad (75)$$

A comparison between Eqs. (72) and (74) indicates that the key species assumption corresponds to the replacement

$$k'_i \to \langle \sigma_i v \rangle. \quad (76)$$

Let us examine under which conditions the concept of a key species is valid. We assume that a sequence of the reactions to form $\mathcal{A}_{i+1}$ from $\mathcal{A}_i$ starts from a reactive collision of a key species $\mathcal{B}_1$ onto $\mathcal{A}_i$ to form an intermediate compound $\mathcal{Z}_{i1}$ such as

$$\mathcal{A}_i + \mathcal{B}_1 \rightleftharpoons \mathcal{Z}_{i1} + \mathcal{D}_{11} + \mathcal{D}_{12} + \cdots$$

In what follows, we consider the case of $n = 2$, in which elementary reactions to form $\mathcal{A}_{i+1}$ from $\mathcal{A}_i$ are written as

$$\mathcal{A}_i + \mathcal{B}_1 \rightleftharpoons \mathcal{Z}_{i1} + \mathcal{D}_{11} + \mathcal{D}_{12} + \cdots, \quad (77)$$

$$\mathcal{Z}_{i1} + \mathcal{B}_2 \rightleftharpoons \mathcal{A}_{i+1} + \mathcal{D}_{21} + \mathcal{D}_{22} + \cdots \quad (78)$$

The overall reaction of a sequence of the reactions (77) and (78) is given by

$$\mathcal{A}_i + \mathcal{B}_1 + \mathcal{B}_2 \rightleftharpoons \mathcal{A}_{i+1} + \mathcal{D}_{11} + \cdots + \mathcal{D}_{21} + \cdots \quad (79)$$

Expressing the steady currents of the elementary reactions by

$$J = k_{i1} c(i) c_1 - \alpha_{i+1,1} c_{\mathcal{Z}_{i1}} c_{\mathcal{D}_{11}} \cdots \quad (80)$$

$$\;\; = k_{i2} c_{\mathcal{Z}_{i1}} c_2 - \alpha_{i+1,2} c(i+1) c_{\mathcal{D}_{21}} \cdots, \quad (81)$$

we obtain the steady current of the overall reaction as

$$J = k_i c(i) c_1 c_2 - \alpha_{i+1} c(i+1) c_{\mathcal{D}_{11}} \cdots c_{\mathcal{D}_{21}} \cdots \tag{82}$$

with the effective rate constants given by

$$\begin{aligned} k_i &= \frac{k_{i1} k_{i2}}{k_{i2} c_2 + \alpha_{i+1,1} \prod_j c_{\mathcal{D}_{1j}}}, \\ \alpha_{i+1} &= \frac{\alpha_{i+1,1} \alpha_{i+1,2}}{k_{i2} c_2 + \alpha_{i+1,1} \prod_j c_{\mathcal{D}_{1j}}}. \end{aligned} \tag{83}$$

Note that the first term $k_{i2} c_2$ in the denominators represents the rate of the forward reaction of (78), whereas the second term $\alpha_{i+1,1} c_{\mathcal{D}_{11}} c_{\mathcal{D}_{12}} \cdots$ represents the rate of the reverse reaction of (77). If the relation

$$\alpha_{i+1,1} c_{\mathcal{D}_{11}} c_{\mathcal{D}_{12}} \cdots \ll k_{i2} c_2, \tag{84}$$

holds, then $k_i' = k_i c_2$ defined by Eq. (75) for $n = 2$ may be approximated to be:

$$k_i' \simeq k_{i1} = \langle \sigma_i v \rangle, \tag{85}$$

and the replacement of (76) is justified. The condition (84) implies that the key–species approximation is valid if the reactive collisions of $\mathcal{B}_2$ onto the intermediate compounds $\mathcal{Z}_{i1}$ to form $\mathcal{A}_{i+1}$ occur faster than the dissociation of $\mathcal{Z}_{i1}$. It is plausible that the condition (84) is met in laboratory experiments of condensation in an inert gas, since the concentrations of $\mathcal{D}_{11}$, $\mathcal{D}_{12}$, $\cdots$, which are produced by the reactions of the key species $\mathcal{B}_1$ with $\mathcal{A}_i$, will satisfy the relation

$$c_{\mathcal{D}_{11}}, c_{\mathcal{D}_{12}}, \cdots \lesssim c_1 \ll c_2$$

if $c_1 \ll c_2$. When there are originally abundant product species $\mathcal{D}_{11}, \cdots$ in the condensation environment such as H_2 in the carbon grain formation from C_2H_2 in C-rich AGB stars, on the other hand, the rate constant $\alpha_{i+1,1}$ must be low enough to compensate high concentrations of the product species.

The situation is essentially unchanged for $n > 2$ as well. Formation of $\mathcal{A}_{i+1}$ from $\mathcal{A}_i$ proceeds through 1) initiation of the sequential reactions by formation of an intermediate compound $\mathcal{Z}_{i1}$ through reactive collisions of the key species $\mathcal{B}_1$ with an i-mer $\mathcal{A}_i$, and 2) a subsequent series of the reactions forming $\mathcal{Z}_{ik}$ through reactive collisions of $\mathcal{B}_k$ ($k = 2, \cdots, n$) with intermediate compounds $\mathcal{Z}_{i,k-1}$. The key–species approximation is valid if the forward reaction for forming $\mathcal{Z}_{ik}$ is faster than its dissociation in each step of the reactions.

To conclude this section, it should be pointed out that the key–species approximation provides one of the effective ways to apply the chemical nucleation rate (38) or (70), which includes the unknown effective rate constants k_i, to actual problems if the condition (84) is confirmed to be satisfied. Although the confirmation requires the knowledge of the rate constants of all elementary reactions in principle, what is required is just to check the inequality like (84), which does not always need their precise values.

7. Concluding remarks

We have developed a kinetic theory of chemical nucleation. The steady nucleation rate (38) will provide a basis of studying astrophysical dust formation, which is usually associated with chemical reactions in the absence of monomers having the same composition as the condensates. It is of course required in the applications to actual situations to take into account of various other effects, for example, the non-LTE effect as discussed by Gail & Sedlmayr (1988), Kozasa et al. (1996) and Patzer et al. (1998) for the circumstellar condensation, and by Yamamoto (1985) for condensation and sublimation in the protoplanetary disk. The present theory has focused on the aspect of chemical reactions in nucleation phenomena, and has derived the nucleation rate without approximation, which we hope has a wide applicability not only in astrophysics but also in other fields. For practical applications and comparisons with experiments, one needs to estimate the rate constants k_i appearing in Eq. (38) or k_{i_*} in Eq. (70). Since it is difficult in general to estimate k_i or k_{i_*} itself, the effective approximations should be sought. The key–species approximation discussed in Sect. 6 is one of those approximations valid if the condition (84) is fulfilled.

There have been two definitions of equilibrium in formulating the nucleation rate. The conventional one is a metastable supersaturated–state of a vapor with the absence of a bulk condensate (e.g., Feder et al. 1966; Abraham 1974), and the other is a saturated state of a vapor coexisting with a bulk condensate (Katz & Wiedersich 1977). We have employed the view of Katz & Wiedersich (1977) and Patzer et al. (1998). Although either of the definitions can be employed so far as the consistency in the theory is preserved, the latter one is clearer because of its reality and stability. The quantities in equilibrium such as the equilibrium concentrations are those for $S = 1$ in the present definition of equilibrium.

It should be pointed out that the present formulation does not depend on a particular cluster model, so is free from the debate on the evaluation of the Gibbs free energy change in the cluster formation. The expression of the minimum work given by Eqs. (41) or (44), which equals the Gibbs free energy change if the clusters and the vapor are of equal temperature and pressure, is a general expression comprised of the volume energy $-(i-1)\ln S$ and the "surface energy". Note that this expression is independent of any cluster model. The "surface energy" term includes only one unknown quantity, $\chi(i)$, the minimum work needed to form an i-mer at a standard pressure P_0. The evaluation of $\chi(i)$ is a subject of the debate, which we have not discussed in this paper. Once $\chi(i)$ is known, the nucleation rate J is straightforwardly calculated from Eq. (38), or more simply from the approximate Eq. (70) if only $\chi(i_*)$ and $\chi''(i_*)$ are known together with the critical size i_*.

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Appendix A: Proof of the fact that $\alpha_{\mathcal{Y}}/\mathrm{k}_{\mathcal{X}}$ is independent of the concentrations.

The proof is given by induction. For $n = 1$, the reaction is an elementary reaction, thus the ratio $\alpha_{\mathcal{Y}}/k_{\mathcal{X}}$ is independent of the concentrations by the postulate stated in Sect. 2.1. For an illustrative purpose, let us examine the case of $n = 2$, for which the steady currents J for the elementary reactions (4) and (5) are given by

$$\begin{aligned} J &= k_1 X B_1 - \alpha_1 Z_1 D_{11} \cdots && \text{(A.1)} \\ &= k_2 Z_1 B_2 - \alpha_2 Y D_{21} \cdots && \text{(A.2)} \end{aligned}$$

Eliminating the concentration Z_1, one obtains the steady current for the overall reaction as

$$J = k_{\mathcal{X}} X B_1 B_2 - \alpha_{\mathcal{Y}} Y F_1 \cdots \quad \text{(A.3)}$$

with

$$k_{\mathcal{X}} = \frac{k_1 k_2}{k_2 B_2 + \alpha_1 D_{11} \cdots}, \quad \alpha_{\mathcal{Y}} = \frac{\alpha_1 \alpha_2}{k_2 B_2 + \alpha_1 D_{11} \cdots}. \quad \text{(A.4)}$$

The ratio of the effective rate constants given by

$$\frac{\alpha_{\mathcal{Y}}}{k_{\mathcal{X}}} = \frac{\alpha_1 \alpha_2}{k_1 k_2} \quad \text{(A.5)}$$

is expressed only by the rate constants of the elementary reactions, thus is independent of the concentrations B_1, B_2 and $F_1, \cdots$.

Now, assume that α/k in the steady current for $n = p$ given by

$$J = k X B_1 \cdots B_p - \alpha Y D_{11} \cdots \quad \text{(A.6)}$$

for the overall reaction

$$\mathcal{X} + \mathcal{B}_1 + \cdots + \mathcal{B}_p \rightleftharpoons \mathcal{Y} + \mathcal{D}_{11} + \cdots \quad \text{(A.7)}$$

is concentration-independent. Splitting the overall reaction for $n = p + 1$ expressed by

$$\mathcal{X} + \mathcal{B}_1 + \cdots + \mathcal{B}_p + \mathcal{B}_{p+1} \rightleftharpoons \mathcal{Y} + \mathcal{F}_1 + \cdots \quad \text{(A.8)}$$

into the following sequential reactions such as

$$\begin{aligned} \mathcal{X} + \mathcal{B}_1 + \cdots + \mathcal{B}_p &\rightleftharpoons \mathcal{Z}_p + \mathcal{D}_{11} + \cdots && \text{(A.9)} \\ \mathcal{Z}_p + \mathcal{B}_{p+1} &\rightleftharpoons \mathcal{Y} + \mathcal{D}_{21} + \cdots, && \text{(A.10)} \end{aligned}$$

one has the steady current as

$$\begin{aligned} J &= k_1 X B_1 \cdots B_p - \alpha_1 Z_p D_{11} \cdots && \text{(A.11)} \\ &= k_2 Z_p B_{p+1} - \alpha_2 Y D_{21} && \text{(A.12)} \end{aligned}$$

according to Eq. (8). Elimination of Z_p leads to

$$J = k_{\mathcal{X}} X B_1 \cdots B_{p+1} - \alpha_{\mathcal{Y}} Y F_1 \cdots \quad \text{(A.13)}$$

with

$$\begin{aligned} k_{\mathcal{X}} &= \frac{k_1 k_2}{k_2 B_{p+1} + \alpha_1 D_{11} \cdots}, \\ \alpha_{\mathcal{Y}} &= \frac{\alpha_1 \alpha_2}{k_2 B_{p+1} + \alpha_1 D_{11} \cdots}. \end{aligned} \quad \text{(A.14)}$$

Thus one has

$$\frac{\alpha_{\mathcal{Y}}}{k_{\mathcal{X}}} = \frac{\alpha_1}{k_1} \cdot \frac{\alpha_2}{k_2}. \quad \text{(A.15)}$$

According to the assumption for $n = p$, α_1/k_1 is independent of the concentrations of $B_1, \cdots, B_p$ and $F_1, \cdots$, and α_2/k_2 is also concentration-independent because the reaction (A.10) is an elementary reaction. Thus, the ratio $\alpha_{\mathcal{Y}}/k_{\mathcal{X}}$ is concentration-independent for $n = p + 1$ as well.

Appendix B: Proof of Eq. (21)

Although one can prove Eq. (21) by substituting Eq. (23) into the LHS of Eq. (21), we give here a simple proof.

Consider the equilibrium between i-mers and a bulk condensate such as

$$\mathcal{A}_i \rightleftharpoons i\mathcal{A}_{\mathrm{s}},$$

then the equilibrium concentration of the i-mers is expressed by

$$\dot{c}(i) = \frac{P_0}{k_{\mathrm{B}}T} \exp\left[-\frac{\chi(i) - i\mu_{\mathrm{s}}}{k_{\mathrm{B}}T}\right] \quad \text{(B.1)}$$

from the equilibrium condition $\dot{\mu}(i) = i\mu_{\mathrm{s}}$. Using Eq. (44), we have

$$\begin{aligned} S^i \dot{c}(i) &= \frac{P_0}{k_{\mathrm{B}}T} \exp\left[i \ln S - \frac{\chi(i) - N\mu_{\mathrm{s}}}{k_{\mathrm{B}}T}\right] \\ &\simeq \frac{P_0}{k_{\mathrm{B}}T} \exp\left[-g(i)\right] \quad (i \gg 1). && \text{(B.2)} \end{aligned}$$

For $S > 1$, $\lim_{i \to \infty} g(i) = -\infty$ results from Eq. (45). Thus, since $c(i)$ is necessarily finite, Eq. (21) has been proved.

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