KINETICS OF ISOTHERMAL HOMOGENEOUS NUCLEATION IN A QUASI-CHEMICAL MODEL

Yu. E. Gorbachev and V. Yu. Kruglov

Many studies have been devoted to the analysis of the kinetics of homogeneous nucleation (see, for instance the survey of Kotake and Glass [1], based on Volmer's and Weber's original work [2]). Most of these studies rely on some variation of the treatment developed by Becker and Döring [3]. Some of their assumptions are rather questionable, however. In addition, calculations based on a classical model agree only qualitatively with experimental data. An analysis of the available experimental studies shows that a satisfactory description is obtained only for condensation in diffusion chambers [4], where the supersaturation varies at a relatively slow rate. The results of experiments performed in free jets and high efficiency heat exchangers disagree significantly with classical-model calculations. The experimental nucleation current may differ from the classical value by as much a 8-9 orders of magnitude [6]. The description of condensation in such systems thus requires a more realistic condensation model.

In this paper we propose converting to new variables [6] in the equations of the quasi-chemical condensation model [7], and separating the system variables into slow and fast ones [8, 9]. Nucleation is then considered as the formation of a quasi-stationary distribution of fast variables. The cutoff between slow and fast variables is identified with a quasi-critical nucleus and defines the nucleus size, which is in certain cases significantly different from the size calculated by classical capillary theory using the Kelvin–Gibbs equation. Analysis of the fast-variable relaxation equations yields the quasi-stationary distribution and a formula for the nucleation current.

When referring to classical theory, we postulate that the quasi-stationary distribution cutoff is the critical nucleus corresponding to maximum cluster potential energy.

1. The Quasi-Chemical Condensation Model and the Equilibrium Cluster-Size Distribution Function. Homogeneous condensation is commonly described by means of a quasi-chemical condensation model [7]. The usefulness of the model is confirmed by direct molecular-dynamics calculations [10]. Analysis of a number of studies on the subject shows that it is possible to neglect the coagulation of even small clusters, because the concentration of monomers is much higher than the concentration of clusters of any size.

Since interaction with g-mers has a negligible effect on the number of monomers at the nucleation stage [11], the monomer concentration is controlled by hydrodynamic processes and is determined by the external macroparameters of the system. Under these conditions, the mean number n_g of clusters of size g per unit volume is defined by

$$\dot{n}_g = I_g - I_{g+1}, \quad I_g = -k_g^- n_g + k_{g-1}^+ n_{g-1} n_1, \quad g = 2, \ldots, \infty, \tag{1}$$

where k_g^+ is the rate constant of formation of clusters of size g out of clusters of size g − 1, and k_g^- is the rate constant of the reverse reaction. If energy relaxation is taken into account, Eqs. (1) must be supplemented by the cluster energy equations; here we consider only isothermal nucleation, however. The association and dissociation constants are related by the equilibrium constant, i.e., $k_g^- = k_g^0 k_g^+$. $k_g^0 = n_{g-1}^e n_1^e / n_g^e$, and the right-hand sides of (1) thus yield the detailed balance, $I_g(n_g^e) = 0$. The equilibrium distribution n_g^e is derived below. Let us use the model $k_g^+ = \alpha g^{2/3} = \alpha_h 4 \pi r_1^2 (kT/2\pi m_1)^{1/2} g^{2/3}$ (α_h is the coefficient of condensation , r_1 and m_1 are the monomer radius and mass, and T is the temperature). Then

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$$I_g = n_1^e \alpha g^{2/3} n_{g-1}^e \left(\widetilde{n}_{g-1} \widetilde{n}_1 - \widetilde{n}_g \right), \qquad \widetilde{n}_g = n_g/n_g^e. \tag{2}$$

To proceed further, we have to analyze the equilibrium cluster-size distribution function. The function n_g^e can be the distribution function corresponding to complete equilibrium in the system, i.e.,

$$n_g^{et} = n_1^e \exp\left(- \Theta g^{2/3} \right), \qquad \Theta = \Theta(T) = 4\pi r_1^2 \sigma/kT \tag{3}$$

(σ is the coefficient of surface tension). The equilibrium constant then becomes $k_g^0 = n_{g-1}^{et} n_1^e / n_g^{et}$. Complete equilibrium implies that the system does not include any super-saturation (S = 1), which may be defined as $S = n_1/n_1^e = \widetilde{n}_1$. Besides its usual thermodynamic derivation, the distribution (3) can also be obtained from the quasi-chemical condensation model equations (1) for a finite system by normalizing and passing to the thermodynamic limit. In addition to the distribution (3), with n_1^e denoting the vapor concentration, it is then also possible to determine the phase separation, i.e., to describe the phase transition [12]. With respect to (3), it is worth noting that the concept of surface tension is inapplicable to the energy of small clusters. In spite of many experimental studies [13] and molecular-dynamics calculations [14], it has been impossible to derive an expression for the cluster free energy based on a unified approach. The available experimental data [15] indicate that surface tension can be used for clusters of size $g > 10^2$. Within our context, the dependence of the free energy on size is not of specific importance, and in order to simplify calculations Eq. (3) may be conveniently used.

Let us examine the transition from one equilibrium state at the temperature T_0 to another state at the temperature T_1. Substituting (3) in (2) and setting $n_g^0 = n_g = n_g^{et}(T_0)$ we get

$$\dot{n}_g \simeq \alpha n_1^e n_1^0 (\widetilde{n}_1 - 1)\, 2 \exp\left(- \Theta_0 g^{2/3} \right)/3 g^{1/3} \tag{4}$$

($\Theta_0 = \Theta(T_0)$). The derivation of (4) is based on an expansion for large g and the fact that $n_{g-1}^{et}/n_g^{et} \sim \exp\left(2\Theta/3 g^{1/3} \right) = O(1)$. According to (4), the relaxation rate $\dot{n}_g$ decreases with increasing g, and when $g \to \infty$, $\dot{n}_g \to 0$. This is consistent with the results of Turner et al. [16], who studied the growth of macroscopic droplets in a free molecular flow. As noted in [11], in most real systems the gas-dynamical parameters, including the monomer concentration n_1, very much more slowly than the relaxation time of the small-cluster concentrations n_g. In this case $\dot{n}_1 \gg \dot{n}_g$ for all g, the condensation is known as frozen, and the kinetics are fairly easy to describe. We are interested in the case when it is possible to define a g_1 for which $\dot{n}_{g_1} \sim \dot{n}_1$. It is then clear from the foregoing that the variables are fast with respect to n_1 for $g < g_1$, and slow for $g > g_1$. The equilibrium distribution function is a general function of the slow variables. If the large-cluster concentration is low relative to the small-cluster concentration, however, an analysis of equilibrium statistical physics [17] yields the equilibrium function

$$n_g^e = n_1 \exp\left(g \ln S - \Theta g^{2/3} \right). \tag{5}$$

The factor before the exponential above is n_1, rather than n_1^e as in (3). This reflects the fact that we are considering not complete equilibrium, but equilibrium at a fixed n_1. The same applies to the equilibrium constant $k_g^0 = n_{g-1}^e n_1/n_g^e$, $k_2^0 = n_1^2/n_2^e$. The basic difference from the classical treatment is that the distribution is used not for clusters smaller than the critical size ($g < g_*$), where $g_* = (2\Theta/3 \ln S)^3$, but for clusters of size $g < g_1$ (g_1 being the separation point between the fast and slow variables). This separation defines more rigorously the domain of the distribution (5), and, as will be seen, yields results significantly different from those of classical analysis.

In order to find g_1, we introduce new variables in the system of equations (1), using the substitution [18, 19]

$$F_g = \widetilde{n}_g/\widetilde{n}_{g-1}, \tag{6}$$

which converts (1) to the form

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$$\dot{F}_g = R_F(g) + E_F(g) + H_F(g); \tag{7}$$

$$R_F(g) = A_F F_g^2 + B_F F_g + C_F, \quad A_F = \left(k_{g+1}^+ - k_g^+\right), \tag{8}$$

$$B_F = -A_F - C_F, \quad C_F = -k_g^- + k_{g+1}^-;$$

$$E_F(g) = k_g^-\left(1 - F_g/F_{g-1}\right) - k_{g+1}^+\left(1 - F_{g+1}/F_g\right) F_g^2; \tag{9}$$

$$H_F(g) = (2\dot{\Theta}/3g^{1/3} - \dot{S}/S)F_g. \tag{10}$$

Equation (10) is derived by an expansion for large g. If E_F and H_F vanish, Eq. (7) becomes the Riccati equation, and we therefore call R_F the Ricatti component. The term E_F (nondiagonal component) is the degree of nonadiabaticity of the F_g variables, and H_F (hydrodynamic component) denotes the effect of the rate of change of the macroscopic (hydrodynamic) parameter on the rate of change of F_g. If we assume that the distribution is sufficiently smooth, i.e. $|F_g/F_{g-1} - 1| \ll 1$, as confirmed by direct numerical calculation, then $E_F \ll R_F, H_F$.

In order to evaluate the Riccati component, we use the same reasoning as in the derivation of (4). Since $n_{g-1}^e/n_g^e \sim O(1)$ we get, for sufficiently large g,

$$R_F \sim 2n_1\alpha/3g^{1/3}. \tag{11}$$

If this value is compared with the hydrodynamic component H_F, then, given the condition

$$g < (2\alpha n_1 S/3\dot{S})^3, \tag{12}$$

the relaxation F_g is determined by the Riccati component R_F, and consequently (7) has the analytic solution

$$F_g = \frac{\exp\left(-t/\tau_F\right)\left(1 - F_g^0\right)C_F/A_F + F_g^0 - C_F/A_F}{\exp\left(-t/\tau_F\right)\left(1 - F_g^0\right) + F_g^0 - C_F/A_F}; \quad \tau_F^{-1}(g) = C_F - A_F, \tag{13}$$

where $F_g^0 = F_g\,(t=0)$. It follows from (13) that when $t \to \infty$, $F_g \to 1$ for $\tau_F > 0$. This entails a quasi-stationary distribution with $I_g = 0$ (see (6)). When $\tau_F < 0$ an analytic solution of (7) is difficult to obtain, since the effect of the nondiagonal component E_F cannot be neglected in that case. The expression for τ_F shows that τ_F changes sign at $g = g_*$; it increases with g, remaining positive for $g < g_*$ and becoming negative in the opposite case. The quantity g_* thus defines the quasi-stationary distribution cutoff, as long as condition (12) is satisfied.

In order to analyze (1) for $g > g_*$, we use another nonlinear substitution [19]:

$$G_g = I_{g+1}/I_g. \tag{14}$$

We get as a result a set of equations similar to (7)-(10), i.e.,

$$\dot{G}_g = R_G(g) + E_G(g) + H_G(g);$$

$$R_G(g) = A_G G_g^2 + B_G G_g + C_G;$$

$$A_G = k_{g+1}^- - k_g^-; \quad B_G = -k_{g+1}^- + k_{g-1}^+ + k_g^- - k_g^+; \quad C_G = k_g^+ - k_{g-1}^+; \tag{15}$$

$$E_G = k_{g-1}^+(1 - G_g/G_{g-1}) - k_{g+1}^-(1 - G_{g+1}/G_g)G_g^2;$$

$$H_G = -G_g \frac{\tilde{n}_{g-1}\tilde{n}_{g+1} - \tilde{n}_g^2}{\left(\tilde{n}_g - \tilde{n}_{g+1}\right)\left(\tilde{n}_{g-1} - \tilde{n}_g\right)}\left(\frac{\dot{S}}{S} - \frac{2}{3}\frac{\dot{\Theta}}{g^{1/3}}\right).$$

If we evaluate the hydrodynamic component H_G for sufficiently large g, we obtain $\dot{S}/S \gg 2\dot{\Theta}/3g^{1/3}$ and, assuming the function $\tilde{n}_g$ is smooth $H_G \simeq -G_g\dot{S}/S$. The component R_G is evaluated

similarly to (11), i.e., $R_G \simeq 2n_1\alpha/3g^{1/3}$. We can accordingly find a number g_S below which the relaxation G_g corresponds to the Riccati component R_G, and above which it corresponds to the hydrodynamic component H_G, viz.,

$$g_s = (2\alpha n_1 S/(3\dot{S}))^3. \tag{16}$$

The derivation of (16) is based on the fact when $g \to g_s$, $G_g \to 1$ (since $G_g \to 1$ for $g < g_S$). Let us examine the condition under which the solution of the Riccati equation for G_g with R_G in the right-hand side tends to unity. The general form of (15) is in that case similar to (13), i.e.,

$$G_g(t) = \frac{\exp(-t/\tau_G)(1-G_g^0)C_G/A_G + G_g^0 - C_G/A_G}{\exp(-t/\tau_G)(1-G_g^0) + G_g^0 - C_G/A_G}; \quad \tau_G^{-1} = C_G - A_G, \tag{17}$$

where $G_g^0 = G_g$ ($t = 0$). Analysis of (17) shows that $\tau_G > 0$ for $g < g_*$ and increases with g; conversely $\tau_G < 0$ for $g > g_*$ (i.e., $G_g \to 1$ when $g > g_*$). An analytic solution cannot be found when $g < g_*$, for the same reason as in the case of the F variables when $g > 0$. Thus, when $g > g_*$, a quasi-stationary distribution is produced in the system, with $I_g = \text{const}$ (see (14)). Its cutoff point is g_S, beyond which the relaxation G_g is determined only by the hydrodynamic parameters.

Since the distribution producing a constant current builds up within a short time, it is reasonable to identify the largest size g_S at which it is established with the phase boundary, and to consider the rate of formation of condensate as the current through a cross section $g = g_S$ in size space.

2. Quasi-Stationary Distribution and Nucleation Current. In order to calculate the quasi-stationary current and cluster-size distribution, we need boundary conditions for the distribution function. The first boundary condition involves the quantity n_{g_S+1}. Since n_{g_S+1} is a slow variable (see Sec. 1), $\tilde{n}_{g_S+1} \sim \exp(-(\Theta_e - \Theta_0)(g_S+1)^{2/3}) \ll 1$ and this leads to a boundary condition similar to that in classical theory, i.e., $\tilde{n}_{g_S+1} = 0$. The other boundary condition is $\tilde{n}_{g_*} = 1$, as the quasi-stable distribution $\tilde{n}_g = 1$ is produced at $g = g_*$. Calculations similar to [3] then yield the following formulas for the quasi-stationary current:

$$I_{st} = \alpha n_1' J(g_S),$$
$$J(g_S) = \sum_{g=g_*}^{g_S} (g^{2/3}n_g^e)^{-1} \simeq \int_{g_*}^{g_S} (x^{2/3}n_x^e)^{-1}\,dx, \tag{18}$$

which are valid for $g_S > g_*$. The formula for I_{st} when $g \leq g_*$ requires further analysis, because the solutions have to be matched in the neighborhood of the point $g = g_*$. Since the quasi-stationary distribution is close to quasi-stable in the range $g < g_*$ (see [1]), the simplest interpolation would be to assume a quasi-stationary distribution throughout the size range $g < g_S$.

Thus, when $g_S > g_*$ the nucleation current given by (18) is virtually the same as in the classical current, but the critical nucleus size g_S defined by (16) may be significantly different from the classical size g_* and its value is dependent on the rate of change of the saturation. This dependence imposes stringent requirements on experimental conditions and makes it necessary to measure some new parameters, specifically S.

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