

## Kinetics of binary nucleation of vapors in size and composition space

Sergey P. Fisenko\* and Gerald Wilemski†

Department of Physics, University of Missouri–Rolla, Rolla, Missouri 65409-0640, USA

(Received 19 June 2004; published 22 November 2004)

We reformulate the kinetic description of binary nucleation in the gas phase using two natural independent variables: the total number of molecules  $g$  and the molar composition  $x$  of the cluster. The resulting kinetic equation can be viewed as a two-dimensional Fokker-Planck equation describing the simultaneous Brownian motion of the clusters in size and composition space. Explicit expressions for the Brownian diffusion coefficients in cluster size and composition space are obtained. For characterization of binary nucleation in gases three criteria are established. These criteria establish the relative importance of the rate processes in cluster size and composition space for different gas phase conditions and types of liquid mixtures. The equilibrium distribution function of the clusters is determined in terms of the variables  $g$  and  $x$ . We obtain an approximate analytical solution for the steady-state binary nucleation rate that has the correct limit in the transition to unary nucleation. To further illustrate our description, the nonequilibrium steady-state cluster concentrations are found by numerically solving the reformulated kinetic equation. For the reformulated transient problem, the relaxation or induction time for binary nucleation was calculated using Galerkin's method. This relaxation time is affected by processes in both size and composition space, but the contributions from each process can be separated only approximately.

DOI: 10.1103/PhysRevE.70.056119

PACS number(s): 64.60.Qb, 05.10.Gg, 64.70.Fx

### I. INTRODUCTION

Multicomponent nucleation of particles in gases plays a significant and sometimes crucial role in many areas of science and technology, including astrophysics, atmospheric science, and nanoparticle production. Binary nucleation is the simplest case of multicomponent nucleation, but one that is very important scientifically. The classical equations of binary nucleation kinetics, first obtained by Reiss [1], describe how clusters containing  $g_a$  and  $g_b$  molecules of species  $a$  and  $b$ , respectively, change in size due to the absorption and emission of single molecules of the two condensable species. These equations permit one to calculate the time evolution of the different cluster concentrations, represented by the distribution function  $f(g_a, g_b)$ . In the approximation of continuous variables, the kinetics equations reduce to a two-dimensional Fokker-Planck equation [2] of the special form

$$\begin{aligned} \partial_t f(g_a, g_b, t) &= \partial_{g_a} [f L_{aa} \partial_{g_a} (\ln f + \beta \Delta \Phi(g_a, g_b))] \\ &\quad + \partial_{g_b} [f L_{bb} \partial_{g_b} (\ln f + \beta \Delta \Phi(g_a, g_b))] \\ &= \partial_{g_a} [-J_a] + \partial_{g_b} [-J_b]. \end{aligned} \quad (1)$$

It follows from the physical interpretation of Eq. (1) that the kinetics of binary nucleation is equivalent to the Brownian motion of a particle moving in a potential defined by the thermodynamic function  $\Delta \Phi(g_a, g_b)$ , the free energy of cluster formation [1]. In Eq. (1) the kinetic coefficients  $L_{aa}$  and  $L_{bb}$  have the explicit form

$$L_{ii} = \frac{p_i A}{\sqrt{2\pi m_i kT}}, \quad (2)$$

where  $p_i$  and  $m_i$  are, respectively, the partial pressure of vapor and mass of molecules of kind  $i$ ,  $T$  is the temperature,  $k$  is Boltzmann's constant,  $A$  is the surface area of the cluster, and  $\beta = 1/kT$ . The free energy surface  $\Delta \Phi(g_a, g_b)$  acts as a thermodynamic barrier over which the growing clusters must pass. As shown by Reiss [1], an essential feature of this surface is a saddle point through which the major nucleation flux generally, although not always, passes. The location of this saddle point is defined by the two equations

$$\frac{\partial \Delta \Phi}{\partial g_a} = \frac{\partial \Delta \Phi}{\partial g_b} = 0, \quad (3)$$

whose solution also determines the critical cluster size  $(g_a^*, g_b^*)$ . Attainment of the critical size effectively defines nucleation, since only supercritical clusters can grow spontaneously. The size of the critical radius  $R_c$  is typically about  $10^{-9}$  m, and usually one finds that  $g_a^* + g_b^* > 30$ , which supports the continuous variable approximation underlying Eq. (1). It should be noted that in some cases the solution of Eq. (3) is not unique.

Here, we will consider the behavior of the kinetic equation (1) in the vicinity of the saddle point of the free energy surface. As a preliminary step, we note that nucleation occurs in the free molecular regime when the two Knudsen numbers ( $\text{Kn}_i = \lambda_i/R$ ) are large,  $\text{Kn}_i \gg 1$ , as is true in most experiments. This implies that the mean free path  $\lambda_i$  of molecular species  $i$  is much larger than the typical droplet radius  $R$ , and that, therefore, there is no correlation between the fluxes of vapor molecules near a cluster. This circumstance greatly simplifies the description of the nucleation kinetics in a binary vapor mixture.

\*Permanent address: A. V. Luikov Heat & Mass Transfer Institute, National Academy of Sciences, Minsk, Belarus.

†Email address: wilemski@umr.edu

Let us note that the equilibrium solution  $f_{eq}$  of the kinetic equation (1), when the fluxes  $J_a$  and  $J_b$  are equal to zero, can easily be found from the right side of Eq. (1):

$$f_{eq}(g_a, g_b) = C \exp[-\beta\Delta\Phi(g_a, g_b)], \quad (4)$$

where  $C$  is the normalization “constant” which may depend on the number densities of the condensable vapor molecules. The determination of the value of  $C$  is still an unsolved problem in the theory of binary nucleation in gases [3].

The boundary conditions for Eq. (1) were introduced by Reiss [1]. They are generalizations of the boundary conditions of the classical theory of nucleation kinetics for the unary vapor [4,5]. According to Ref. [1], the boundary conditions are that  $f(g_a, g_b)$  is the equilibrium distribution function for small clusters, and  $f(g_a, g_b)=0$  for relatively large clusters (in comparison with the critical size). For a two-dimensional partial differential equation, like Eq. (1), these boundary conditions are not adequate for finding a correct solution of the equation. They must be supplemented by reflecting boundary conditions that prevent the cluster flux from spreading into regions of negative  $g_a$  and  $g_b$  values. It should be noted that the correct boundary conditions for Eq. (1) were given and used for the numerical solution in earlier work [6].

In the past, the kinetic equation for binary nucleation has been obtained in terms of the variables  $(g_a, g_b)$  [1,7]. As we will show, some features of binary nucleation kinetics can be more conveniently investigated by means of the independent variables  $g, x$ . Here,  $g = g_a + g_b$  is the total number of molecules in the cluster, and  $x = g_b/g$  is the molar composition of the cluster. Moreover, the usage of these variables opens up an alternative to the standard method for the development of the theory of multicomponent nucleation kinetics.

From the point of view of further theoretical investigation, it is useful also to separate “unstable” and “stable” variables [8] in the kinetic equation. In nucleation studies, the variable  $g$  is the “unstable” variable and  $x$  is the “stable” one; this classification corresponds with the shape of the cluster free energy surface (see Fig. 1) at the saddle point. The direction of negative curvature is associated with the unstable (or unbounded) variable, while the direction of positive curvature is related to the stable (or bounded) variable. It is of interest to note that for many problems of physics, the behavior of the stable variable is the most interesting aspect. In nucleation studies, we have the opposite situation.

Numerical solution of the binary nucleation kinetics equations is now a relatively facile problem with modern computers for either steady-state or transient kinetics [7,9], provided the critical size is not too big. The general problem that remains is how one can extract some physical insight from the numerical results. One aim of this paper is to develop several criteria that will allow for accurate qualitative description or classification of the main features of binary nucleation kinetics in gases. Such criteria should be useful tools for both computational and experimental research.

In Sec. II the explicit form of the kinetic equation of binary nucleation is presented in the variables  $g$  and  $x$ . The qualitative estimations are made in Sec. III, where the idea is introduced of two induction times, one for the size dynamics

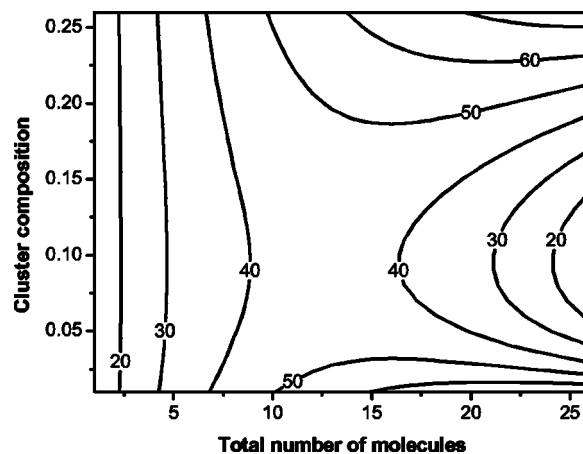


FIG. 1. Contour plot of the dimensionless free energy of cluster formation  $\beta\Delta\Phi(g, x)$  for the binary nucleation of a mixture of *m*- and *o*-xylene. The saddle point values are  $\beta\Delta\Phi(g^*, x^*)=42.57$ ,  $g^*=12.54$ ,  $x^*=0.082$ ; for comparison the kinetic composition is  $x_k=0.486$ . The supersaturations are  $S_a=5$ ,  $S_b=3.75$ ; physical properties are taken from Ref. [12].

and one for the composition dynamics, governing the relaxation to steady state. The analytical evaluation of the steady-state nucleation rate and some numerical results are presented in Sec. IV. The quantitative estimate of the two induction times is made in Sec. V. The main conclusions are summarized in Sec. VI. A few preliminary results of this investigation have been published already [10].

## II. KINETIC EQUATION OF BINARY NUCLEATION IN VARIABLES $g$ AND $x$

To preserve the physical meaning of the distribution function in Eq. (1), the distribution function  $\varphi(g, x, t)$  relative to the variables  $g$  and  $x$  should be defined as [2]

$$f(g_a, g_b, t) dg_a dg_b = \varphi(g, x, t) dg dx. \quad (5)$$

The saddle point on the surface of the free energy of cluster formation,  $\Delta\Phi(g, x)$  can be found as the simultaneous solution of the two equations [11]

$$\frac{\partial\Delta\Phi}{\partial g} = \frac{\partial\Delta\Phi}{\partial x} = 0. \quad (6)$$

We denote the solutions of Eq. (6) as  $g^*$  and  $x^*$ . As an illustration, for a vapor mixture of *m*- and *o*-xylene, in Fig. 1 the contour lines of constant free energy of cluster formation are shown near the saddle point of this surface [12]. This saddle point has the lowest value of the free energy of cluster formation along the ridge of maxima that separates sub- and supercritical nuclei.

If we treat  $g$  and  $x$  as continuous variables, the kinetic equation for  $\varphi(g, x, t)$  can be written as

$$\partial_t \varphi(g, x, t) = -[\partial_g J_g + \partial_x J_x], \quad (7)$$

where the flux components are defined as

$$J_g = (L_{aa} + L_{bb})F_g + a(g,x)F_x, \quad J_x = a(g,x)F_g + b(g,x)F_x, \quad (8)$$

and the thermodynamic “force” components are

$$F_g = -(\partial_g + \beta \partial_g \Delta \Phi - g^{-1})\varphi, \quad F_x = -(\partial_x + \beta \partial_x \Delta \Phi)\varphi. \quad (9)$$

We also have the following relations among the “new” and “old” fluxes:

$$J_g = g(J_a + J_b), \quad J_x = (1-x)J_b - xJ_a. \quad (10)$$

The flux expressions (8) have a pleasing symmetry, reminiscent of the Onsager reciprocal relations [13]. The cross-effect terms that couple the fluxes and forces in size ( $g$ ) and composition ( $x$ ) space have the same coefficient  $a(g,x)$ . In the previous formulas, we use the notation

$$a(g,x) = \frac{L_{bb}(1-x) - xL_{aa}}{g}, \quad b(g,x) = \frac{L_{bb}(1-x)^2 + L_{aa}x^2}{g^2}. \quad (11)$$

It follows from the physical interpretation of the kinetic equation (7) that the sum  $(L_{aa} + L_{bb})$  is the coefficient of Brownian diffusion in the cluster size space and  $b(g,x)$  is the coefficient of Brownian diffusion in the cluster composition space. The latter is always positive and inversely proportional to  $g^2$ . The mean square amplitude of fluctuations in the cluster composition is directly proportional to the Brownian diffusion coefficient in composition space. Therefore, for larger clusters the average amplitude of such fluctuations will be smaller.

For binary nucleation, we introduce the additional characteristic composition  $x_k$ . The explicit expression for  $x_k$  is

$$x_k = \frac{L_{bb}}{L_{aa} + L_{bb}}. \quad (12)$$

The parameter  $x_k$  is of a purely kinetic nature because it depends only on the partial pressures of the vapors and the molecular masses. For an arbitrary size  $g$ , if a cluster has a molar composition equal to  $x_k$ , the coefficient  $a(g,x_k)=0$ . Moreover, at this composition the coefficient of Brownian diffusion in the composition space is a minimum,  $b(g,x_k) \Rightarrow \min$ . For relatively high vapor supersaturations, it is easy to show that the molar composition of a large cluster is about equal to  $x_k$ .

Let us now find the equilibrium solution of the kinetic equation (7). Substituting the expression  $\varphi(g,x) = w(g,x)\exp[-\beta\Delta\Phi(g,x)]$  into Eq. (8), it is easy to see that to satisfy the conditions  $J_g = J_x = 0$  as well as Eq. (5), we must put

$$w(g,x) = Cg. \quad (13)$$

Therefore, the equilibrium function  $\varphi_{eq}(g,x)$  has the form

$$\varphi_{eq}(g,x) = Cg \exp[-\beta\Delta\Phi(g,x)]. \quad (14)$$

Based on the form of Eq. (14), we can represent the nonequilibrium distribution function [4,5] as

$$\varphi(g,x) = Cg \exp[-\beta\Delta\Phi(g,x)]y(g,x), \quad (15)$$

where  $y(g,x)$  is a function changing in the range [0,1]. Equation (15) defines the function  $y$  [4,5].

After substituting Eq. (15) into Eqs. (8) and (9), we have the following formulas for the fluxes:

$$J_g = -\varphi_{eq}[(L_{aa} + L_{bb})\partial_g y(g,x) + a(g,x)\partial_x y(g,x)], \quad (16)$$

$$J_x = -\varphi_{eq}[a(g,x)\partial_g y(g,x) + b(g,x)\partial_x y(g,x)]. \quad (17)$$

For the function  $y(g,x)$ , the boundary conditions are the following:

$$y = \begin{cases} 1 & \text{for small values of } g \text{ at all } x, \\ 0 & \text{for large values of } g, \quad g \gg g^*. \end{cases}$$

The total nucleation rate  $I$ , which is an observable quantity, can be expressed as the integral of  $J_g$  over all the possible cluster compositions

$$I = \int_0^1 J_g(g,x) dx. \quad (18)$$

In formulas (15)–(18) the time variable  $t$  was omitted for simplicity.

For a two-dimensional (2D) problem, two supplementary boundary conditions should be added. We follow the ideas presented in earlier work [6] and put the boundary conditions on two lines. These lines create a closed domain in cluster size and composition space together with Reiss's boundary conditions. We have the following new boundary conditions:

$$\vec{J} \cdot \vec{n} = 0, \quad (19)$$

where  $\vec{n}$  is the normal vector to these two lines. The physical meaning of the new boundary conditions is obviously that the particle flux across these lines is zero. For the variables  $(g,x)$  in the general case the equations of these two lines are  $x=1$  and  $x=0$ . It is important to note that for these full boundary conditions, the total steady-state nucleation rate  $I$ , Eq. (18), does not depend on  $g$ .

### III. QUALITATIVE CONSIDERATIONS

It is very useful to make qualitative estimates [14] of the key parameters characterizing the kinetics of binary nucleation. Let us determine the size of the domain in the cluster and composition space near the saddle point, where the Brownian motion of newly formed clusters occurs. The basic idea is that thermal fluctuations can change the free energy of cluster formation only by several units of  $kT$  in this domain. Therefore, in the cluster size space, the characteristic size  $\delta g$  of this domain can be estimated as

$$\Delta g \sim \sqrt{1/|\beta|\partial_{gg}^2 \Delta \Phi(g^*,x^*)|}, \quad (20)$$

and, in the composition space, the characteristic size  $\Delta x$  of this domain can be estimated as

$$\Delta x \sim \sqrt{1/|\beta|\partial_{xx}^2 \Delta \Phi(g^*,x^*)|}. \quad (21)$$

From the analysis of the expressions for flows (16) and (17), let us obtain two dimensionless parameters characteristic of

the binary nucleation kinetics. These parameters involve both the kinetic and thermodynamic properties of the system. The first parameter, denoted as  $Z$ , arises from the comparison of terms in Eq. (16). It can be written as

$$Z = \frac{a(g^*, x^*) \Delta g}{(L_{aa} + L_{bb}) \Delta x} = \frac{(x_k - x^*)}{g^*} \sqrt{\frac{\partial_{xx}^2 \Delta \Phi(g^*, x^*)}{-\partial_{gg}^2 \Delta \Phi(g^*, x^*)}}. \quad (22)$$

If  $Z \ll 1$ , it is possible to neglect the contribution of the second term in expression (16).

As an illustration, it should be mentioned that for the thermodynamic conditions shown in Fig. 1, the parameter  $Z = 2.85$ , mainly due to the large value of  $\partial_{xx} \Delta \Phi(g^*, x^*)$  in comparison with  $\partial_{gg} \Delta \Phi(g^*, x^*)$ . We can expect that when  $\partial_{xx} \Delta \Phi(g^*, x^*) \sim \partial_{gg} \Delta \Phi(g^*, x^*)$ , the parameter  $Z$  will be much smaller than unity.

The second parameter, denoted by  $H$ , arises from the qualitative analysis of expression (17) and is written as

$$H = \frac{a(g^*, x^*) \Delta x}{b(g^*, x^*) \Delta g} = \frac{(L_{aa} + L_{bb})(x_k - x^*) g^*}{(L_{bb}(1 - x^*)^2 + L_{aa} x^{*2})} \sqrt{\frac{-\partial_{gg}^2 \Delta \Phi(g^*, x^*)}{\partial_{xx}^2 \Delta \Phi(g^*, x^*)}}. \quad (23)$$

When  $Z \ll 1$  and  $H \ll 1$ , it is possible to neglect the cross-effect terms in the right-hand sides of Eqs. (16) and (17). These cross-effect terms are responsible for the coupling between the kinetic processes in the two spaces. For the thermodynamic conditions used for Fig. 1, the parameter  $H = 0.14$ .

Let us demonstrate the origin of the third parameter for binary nucleation more physically. The characteristic time  $\tau_g$  of binary nucleation in the cluster size space can be estimated now as

$$\tau_g \sim \frac{\Delta g^2}{L_{aa} + L_{bb}}. \quad (24)$$

The characteristic time  $\tau_g$  is the exact analogy of the characteristic time for unary nucleation. For binary nucleation, we have to introduce the additional characteristic time  $\tau_c$ , which defines the temporal scale of the Brownian process in the composition space

$$\tau_c \sim \frac{\Delta x^2}{b(g^*, x^*)}. \quad (25)$$

The ratio between characteristic times  $\tau_c / \tau$  is equal to

$$\frac{\tau_c}{\tau_g} \sim \frac{\Delta x^2 (L_{aa} + L_{bb})}{\Delta g^2 b(g^*, x^*)} = \frac{H}{Z}. \quad (26)$$

This ratio of time scales determines the third parameter of binary nucleation, denoted by  $W$ , as

$$W = \frac{H}{Z} = \frac{(L_{bb} + L_{aa})(g^*)^2}{(L_{bb}(1 - x^*)^2 + L_{aa} x^{*2})} \frac{|\partial_{gg}^2 \Delta \Phi(g^*, x^*)|}{\partial_{xx}^2 \Delta \Phi(g^*, x^*)}. \quad (27)$$

If  $W \ll 1$ , we have the following picture of the binary nucleation kinetics. The Brownian diffusion in the composition space is the fastest process. The Brownian diffusion in the

cluster size space is a relatively slow process. For the thermodynamic conditions used for creation of Fig. 1 (supersaturation  $S_a = 5$ ,  $S_b = 3.75$ ) the parameter  $W = 0.05$ . If the parameter  $W \gg 1$ , we can expect some effects directly related to ridge crossing [15,16]. Indeed, for the numerical results that exhibited ridge crossing nucleation kinetics [9], the parameter  $W \cong 161$ . Formal mathematical analysis of expressions (16) and (17) leads to the same result concerning the parameter  $W$ . For the domain defined by the condition of  $3kT$  difference between the saddle point and the domain boundaries in Fig. 1, the characteristic nucleation time  $\tau \sim 2 \times 10^{-6}$  s and, correspondingly,  $\tau_c$  is about 20 times smaller. We will discuss this problem in more detail below.

For qualitative estimation of the binary nucleation kinetics, it is also useful to estimate the ratio of the fluxes  $J_x / J_g$ . In the general case, this ratio can be expressed as

$$J_x / J_g \sim \frac{b(g^*, x^*) \Delta g (1 + H)}{(L_{aa} + L_{bb}) \Delta x (1 + Z)} = \frac{Z(1 + H) \Delta x}{H(1 + Z) \Delta g}. \quad (28)$$

For the free energy surface plotted in Fig. 1, we have that  $J_x / J_g \ll 1$ , so the flux, viewed as a vector, is practically parallel to the  $g$  axis. We can expect that in the majority of cases the inequality  $J_x / J_g \ll 1$  is valid, because usually  $(\Delta x / \Delta g) \ll 1$ .

Using Eqs. (10) it is also easy to find the formally exact expression

$$J_x / J_g = (x_\phi - x) / g, \quad (29)$$

where  $x_\phi = \tan \phi / (1 + \tan \phi)$ . The angle  $\phi$ , defined by  $\tan \phi = J_b / J_a$ , is itself a function of  $x$  and  $g$  that can be determined to at least a good approximation using the theory of Li and Nishioka [17]. At the saddle point, this angle defines the direction of the principal nucleation flux in accord with Stauffer's well-known results [18]. Beyond the critical size, along the principal growth path,  $\phi$  will equal Stauffer's growth angle  $\psi$ . For clusters much larger than the critical size, Stauffer showed that the limiting composition  $x_G$  attained by the growing droplets under conditions of constant vapor supersaturation would satisfy the equation

$$\tan \psi = \frac{L_{bb}[1 - 1/S_b(x_G)]}{L_{aa}[1 - 1/S_a(x_G)]} = \frac{x_G}{1 - x_G}, \quad (30)$$

where  $S_a(x)$  and  $S_b(x)$  are the supersaturations with respect to a liquid mixture of composition  $x$ . Thus, for large  $g$ , we have the asymptotic result  $x_G = x_\phi(x_G, g)$  for all  $g$ . In the limit of high supersaturations, it is easy to see from Eq. (30) that  $x_G$  reaches the limiting value  $x_k$ , defined earlier. It follows from expression (29) that the path defined by the equation  $x = x_\phi(x, g)$  is the "attractive" asymptotic line for all growing binary clusters.

#### IV. STEADY-STATE NUCLEATION RATE

In this section we consider the special case of steady-state kinetics of binary nucleation, taking into account the results of our qualitative analysis. While a full solution of Eqs. (7) and (8) is actually more difficult in terms of the  $(x, g)$  variables than with the  $(g_a, g_b)$  variables, our formulation readily

motivates a simple and useful approximation that is suggested by the qualitative physical difference between the  $x$  and  $g$  variables. We consider the case for which  $\Delta x/x^*$  is so small that the inequality  $W \ll 1$  is valid. In this case, we use the following approximation for the distribution function  $\varphi(g, x)$ :

$$\varphi(g, x) = h(g) \delta(x - x^*). \quad (31)$$

Expression (31) is a good approximation when the pass on the free energy surface is very narrow near the saddle point. Then, after integrating Eq. (7) over all the possible  $x$  values and neglecting a small term proportional to  $a(g, x^*) \partial_x \Delta \Phi(g, x^*)$ , which vanishes at the saddle point, we obtain a one-dimensional kinetic equation. This equation coincides exactly with Zeldovich's kinetic equation [4]. After calculations that are standard for nucleation theory, the expression for the total nucleation rate  $I$  can be written as

$$I = C_1(L_{aa} + L_{bb}) \exp[-\beta \Delta \Phi(g^*, x^*)] \sqrt{\frac{\alpha}{\pi}}, \quad (32)$$

where

$$\alpha = -\frac{\beta}{2} \partial_{gg} \Delta \Phi(g^*, x^*). \quad (33)$$

Note that if  $p_a \rightarrow 0$  or  $p_b \rightarrow 0$  (implying  $x \rightarrow 0$  or  $x \rightarrow 1$ ) expression (32) reduces to the classical rate expression for unary nucleation kinetics. For the approximation (31), the fluxes in the composition and cluster size spaces satisfy the relationship  $J_x/J_g = 0$ .

For the domain with the  $3kT$  difference and for the conditions presented in Fig. 1,  $\Delta x/x^*$  is equal to 0.6; although the width of the valley is not as narrow as the approximation assumes, Eq. (32) still has considerable practical utility. We compared the values predicted using Eq. (32) with those given by Stauffer's rate formula [18], which is known to be quite accurate, except in the unary limit [9]. The calculations were made for the ethanol-hexanol system [9] for a wide range of vapor partial pressures. We found that rates from Eq. (32),  $I(32)$ , were usually greater than or equal to Stauffer's rate  $I_S$ ,  $0.5 \leq I(32)/I_S \leq 15$ , for conditions under which unary nucleation would not predominate. When unary nucleation does predominate, Eq. (32) has the merit of reducing properly to the correct unary rate. Thus, this relatively simple expression may have some utility for estimating nucleation rates in binary systems to within an order of magnitude of the correct numerical value.

#### A. Numerical simulation of the steady-state kinetics of binary nucleation

For the thermodynamic conditions used for the creation of Fig. 1, the numerical solution of the 2D kinetic equation (7) with full boundary conditions was obtained by the relaxation method for the rectangular domain  $\Omega$ . With reference to the geometry of Fig. 1, the boundaries of this domain are defined as follows. The boundaries parallel to the  $g$  axis above and below the saddle point are specified by the two lines  $x = x_1$  and  $x = x_2$ , where  $x_1$  and  $x_2$  are constants defined by the equation

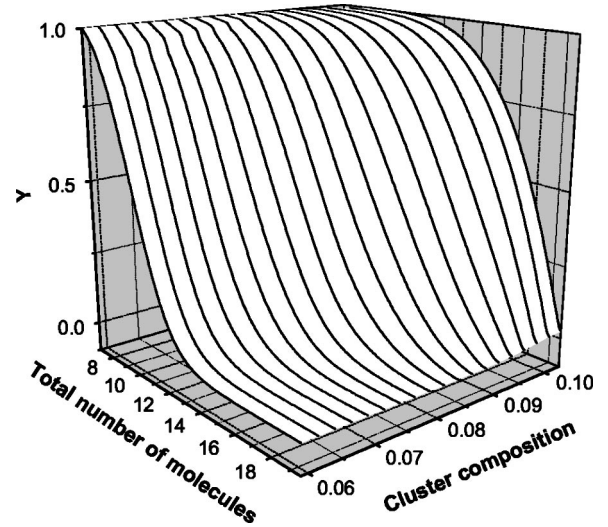


FIG. 2. A three-dimensional view of the dimensionless function  $y$  for the conditions of Fig. 1.

$$\beta[\Delta \Phi(g^*, x_i) - \Delta \Phi(g^*, x^*)] = 3, \quad i = 1, 2. \quad (34)$$

The boundaries parallel to the  $x$  axis to the right and left of the saddle point are specified by the two lines  $g = g_1$  and  $g = g_2$ , where  $g_1$  and  $g_2$  are constants defined by the equation

$$\beta[\Delta \Phi(g^*, x^*) - \Delta \Phi(g_i, x^*)] = 3, \quad i = 1, 2. \quad (35)$$

The boundary conditions on this rectangle were defined in the manner proposed previously [6]: For  $g = g_1$ ,  $y(g_1, x) = 1$ , and for  $g = g_2$ ,  $y(g_2, x) = 0$ . Along the lines  $x = x_1$  and  $x = x_2$  the following conditions hold:

$$\partial_x [y(g, x_i)] = 0, \quad i = 1, 2. \quad (36)$$

The boundary conditions (36) mean that clusters cannot leave this region during nucleation. From the mathematical point of view, these boundary conditions permit the function  $y$  to change continuously from 0 to 1 along these domain boundaries. The relaxation method was used for solving this boundary problem. We emphasize that the grid scheme of the equation was created in such manner in order to maintain the conservative nature of Eq. (7). The result of this calculation, a 3D plot of the slowly changing function  $y(g, x)$ , is presented in Fig. 2. For  $x = x^*$  and  $g = g^*$ , the value  $y = 0.5$  is found [19,20]. A contour plot of  $y(g, x)$  is shown in Fig. 3.

It can be concluded from Fig. 2 that establishment of the steady-state regime is faster for small values of the variable  $x$ . We see that the function  $y$  decays to zero at smaller values of  $g$  when  $x$  is smaller than when  $x$  is larger. Since more time is needed to produce larger cluster sizes, the transition to the steady state will be shorter for smaller values of  $g$ . The calculation of a characteristic time of steady-state binary nucleation is presented in the next section.

#### V. CALCULATION OF RELAXATION TIME OF BINARY NUCLEATION

Qualitative estimates of the characteristic times needed to establish steady-state binary nucleation have been made in

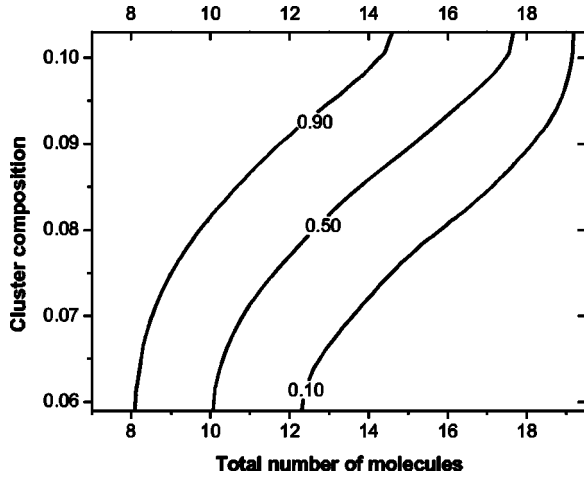


FIG. 3. The same dimensionless function  $y$  as in Fig. 2, but shown as a contour plot.

Sec. III. Here we make quantitative calculations of the relaxation times of the binary nucleation kinetics by the Galerkin method [21]. The full boundary conditions are used below.

For our purpose, the slowly changing function  $y(g, x)$  may be represented as

$$y(g, x) = y_{st}(g, x) + A(t) \sin[\gamma(g)] \sin^2[\mu(x)] \quad (37)$$

where  $y_{st}(g, x)$  is the steady-state solution of Eq. (6) with boundary conditions (36) and

$$\gamma(g) = \pi(g - g^* + 0.5\Delta g)/\Delta g, \quad (38)$$

$$\mu(x) = \pi(x - x^* + 0.5\Delta x)/\Delta x. \quad (39)$$

The second term in expression (37) exactly satisfies the zero boundary conditions for small and large  $g$ , and the condition  $\vec{J} \cdot \vec{n} = 0$  for the other two boundaries of the domain, which we consider as straight lines.

Following the application of Galerkin's method [21], we define the inner product of functions  $f(g, x)$  and  $h(g, x)$  as follows:

$$\langle fh \rangle = \int \int_{\Omega} \varphi_{eq} f h \, dg \, dx. \quad (40)$$

The domain  $\Omega$  was described in the previous section. After substituting expression (37) into Eqs. (7)–(9), we multiply both sides of Eq. (7) by the control function  $\sin[\gamma(g)] \sin[\mu(x)]$ , and integrate each side of the equation over the domain  $\Omega$ . As a result of this standard procedure for Galerkin's method, we find the following equation for the evolution of the amplitude  $A(t)$ :

$$k_0 \partial_t A = -\pi^2 A [k_1 + k_2 + k_3]. \quad (41)$$

The solution of Eq. (41) has the form

$$A(t) = A_0 \exp[-t/\tau], \quad (42)$$

where  $A_0$  is the initial value of this amplitude, which can be arbitrary. The relaxation time  $\tau$  is equal to

$$\tau = \frac{k_0}{\pi^2 [k_1 + k_2 + k_3]}, \quad (43)$$

where the following definitions apply:

$$k_0 = \langle \sin^2[\gamma(g)] \sin^3[\mu(x)] \rangle, \quad (44)$$

$$k_1 = \frac{(L_{aa} + L_{bb})}{\Delta g^2} \langle \cos^2[\gamma(g)] \sin^3[\mu(x)] \rangle, \quad (45)$$

$$k_2 = \frac{2}{\Delta x^2} \langle b(g, x) \sin^2[\gamma(g)] \sin[\mu(x)] \cos^2[\mu(x)] \rangle, \quad (46)$$

$$k_3 = \frac{1}{2\Delta x \Delta g} \langle a(g, x) \sin[2\gamma(g)] \sin[\mu(x)] \sin[2\mu(x)] \rangle. \quad (47)$$

All integrals are nonlinear functions of  $\Delta x$  and  $\Delta g$ . We emphasize that the cross effect between spaces, related to the coefficient  $a(g, x)$  in the kinetic equation (7), gives the contribution to the relaxation time described by  $k_3$ .

Let us introduce  $\tau_g$ , which describes the main contribution for relaxation in the cluster size space

$$\tau_g = \frac{k_0}{\pi^2 k_1}, \quad (48)$$

and in the limit of unary nucleation we must have the equality  $\tau = \tau_g$ . Correspondingly, the relaxation time  $\tau_c$  for composition space is [cf. expression (25)]

$$\tau_c = \frac{k_0}{\pi^2 k_2}, \quad (49)$$

and in the limit of unary nucleation, we must have the result  $\tau_c \rightarrow \infty$ . This follows because the relaxation time is inversely proportional to the collision frequency of the dilute component. As this species concentration is reduced to zero, the collision frequency vanishes, and  $\tau_c$  diverges. If we neglect the small contribution from the  $k_3$  term, which vanishes anyway in the unary limit, we can use the definitions (48) and (49) to rewrite Eq. (43) as

$$\frac{1}{\tau} = \frac{1}{\tau_g} + \frac{1}{\tau_c}, \quad (50)$$

which has the familiar structure for parallel relaxation processes. Interestingly, the ratio  $k_1/k_2 = \tau_c/\tau_g$  can be represented by means of the parameter  $W$ , defined in Sec. III. This allows the alternative expression  $\tau = \tau_g W / (1 + W)$ . We can consider the expression (43) for  $1/\tau$  as an approximation of the lowest eigenvalue of Eq. (7) with full boundary conditions.

It is useful to obtain approximate, analytical results for the integrals (44)–(47). Obviously, the value of the free energy of cluster formation at the saddle point does not explicitly affect the value of  $\tau$  as given by our expressions, although there is an implicit relationship since from classical theory  $\Delta\Phi^*$  is proportional to  $g^*$  and a nonlinear function of  $x^*$ . Hence, small values of  $\Delta\Phi^*$  imply small values of  $g^*$ , etc. If

the integrals are estimated very roughly using the mean value theorem (e.g., with mean values of  $\sin^2$  and  $\cos^2$  equal to 0.5), we have

$$\tau \approx \frac{1}{\pi^2 \left( \frac{L_{aa} + L_{bb}}{\Delta g^2} + \frac{2[L_{aa}x^{*2} + L_{bb}(1-x^*)^2]}{\Delta x^2 g^{*2}} \right)}. \quad (51)$$

We see that the approximate forms (50) and (51) separate the relaxation processes in the cluster size and composition spaces. In previous analytical work [22–24] on this problem, such a separation was not considered, although, in retrospect, there is clear evidence for the two processes in numerical simulations of transient binary nucleation kinetics [25]. For practical purposes, it is possible to use the following formulas for  $\Delta g$  and  $\Delta x$  (obtained for  $3kT$  difference from the saddle point in the parabolic expansion of the free energy of cluster formation):

$$\Delta g = \sqrt{6/\beta |\partial_{gg}^2 \Delta \Phi(g^*, x^*)|} \quad (52)$$

and

$$\Delta x = \sqrt{6/\beta \partial_{xx}^2 \Delta \Phi(g^*, x^*)}. \quad (53)$$

## VI. CONCLUSIONS

For the theoretical investigation of some features of binary nucleation kinetics in gases, the transformation to a different set of natural variables, the total number of molecules  $g$  and the composition  $x$ , was made. This transformation, which has a clear physical meaning, helps to separate the processes in the cluster size and composition space. In particular, we obtained expressions for the coefficients of Brownian diffusion in both the composition and cluster size space, respectively, as  $[L_{bb}(1-x)^2 + L_{aa}x^2]/g^2$  and  $(L_{aa} + L_{bb})$ . The coefficient of Brownian diffusion in composition space has its minimum value when  $x=x_k$ . This composition  $x_k$  is

defined by purely kinetic factors,  $x_k=L_{bb}/(L_{aa}+L_{bb})$ .

Three independent dimensionless parameters useful for the characterization of binary nucleation kinetics in gases have been obtained in the frame of our approach:  $Z$  and  $H$ , expressions (22) and (23), and their ratio  $W=H/Z$ . These parameters include both thermodynamic and kinetic factors and permit one to identify the main physical characteristics of any gas phase binary nucleation process.

For the case when  $W \ll 1$  (i.e., Brownian diffusion in the composition space is much faster than Brownian diffusion in the cluster size space), analytical expressions for the total nucleation rate were obtained with roughly the same accuracy as the classical ones [1,15,18]. Note that if the partial pressure of either component goes to zero (implying  $x \rightarrow 0$  or  $x \rightarrow 1$ ), our simple expression, Eq. (32), reduces to the classical rate expression for unary nucleation kinetics. In other words, in our approach the common failure of binary nucleation kinetics to convert smoothly to unary nucleation does not arise. For steady-state binary nucleation kinetics, a numerical solution was found using the full set of boundary conditions. Numerical results of the full 2D calculation of binary nucleation kinetics were presented in Figs. 2 and 3.

The characteristic relaxation times for binary nucleation kinetics in cluster size space  $\tau_g$  and in composition space  $\tau_c$  have been estimated in expressions (24) and (25). For the full boundary conditions in the cluster size and composition space, the calculation of the relaxation time of binary nucleation was made using Galerkin's method. The contributions of the relaxation processes in cluster size and composition space can be separated approximately in expressions (50) and (51).

## ACKNOWLEDGMENTS

This work was supported by the Engineering Physics Program of the Division of Materials Sciences and Engineering, Basic Energy Sciences, U.S. Department of Energy. G.W. thanks Paul Parris for several helpful discussions.

- 
- [1] H. Reiss, *J. Chem. Phys.* **18**, 840 (1950).  
 [2] H. Risken, *The Fokker-Planck Equation* (Springer, Berlin, 1984).  
 [3] G. Wilemski and B. E. Wyslouzil, *J. Chem. Phys.* **103**, 1127 (1995).  
 [4] Y. B. Zeldovich, in *Chemical Physics and Hydrodynamics: Selected Works*, edited by J. P. Ostriker, G. I. Barenblatt, and R. A. Sunyaev (Princeton University Press, Princeton, NJ, 1992), Vol. 1, p. 120.  
 [5] J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).  
 [6] A. N. Rogozhnikov, S. P. Fisenko, and S. I. Shabunya, *Vysokochist. Veshchestva* **5**, 126 (1989) [*High-Purity Substances* **4**, 833 (1990)].  
 [7] S. P. Fisenko, Heat & Mass Transfer Institute, Minsk, Preprint No. 35, 1987 (unpublished) (in Russian).  
 [8] H. Haken, *Synergetics: An Introduction* (Springer, Berlin, 1983).  
 [9] B. E. Wyslouzil and G. Wilemski, *J. Chem. Phys.* **103**, 1137 (1995).  
 [10] S. P. Fisenko and G. Wilemski, in *Nucleation and Atmospheric Aerosols 2000*, edited by B. N. Hale and M. Kulmala, AIP Conf. Proc. No. 534 (AIP, Melville, NY, 2000), p. 343.  
 [11] B. N. Hale and G. Wilemski, *Chem. Phys. Lett.* **305**, 263 (1999).  
 [12] P. Mirabel and J. L. Katz, *J. Chem. Phys.* **67**, 169 (1977).  
 [13] L. Onsager, *Phys. Rev.* **37**, 405 (1931); **38**, 2265 (1931).  
 [14] V. P. Krainov, *Qualitative Methods in Physical Kinetics and Hydrodynamics* (American Institute of Physics, New York, 1992).  
 [15] H. Trinkaus, *Phys. Rev. B* **27**, 7372 (1983).  
 [16] J.-S. Li, I. L. Maksimov, and G. Wilemski, *Phys. Rev. E* **61**, R4710 (2000).  
 [17] J.-S. Li and K. Nishioka, *J. Chem. Phys.* **110**, 5866 (1999).

- [18] D. Stauffer, *J. Aerosol Sci.* **7**, 314 (1974).
- [19] B. E. Wyslouzil and G. Wilemski, *J. Chem. Phys.* **110**, 1202 (1999).
- [20] G. Wilemski, *J. Chem. Phys.* **110**, 6451 (1999).
- [21] C. A. J. Fletcher, *Computational Galerkin Method* (Springer, New York, 1984).
- [22] G. Wilemski, *J. Chem. Phys.* **62**, 3772 (1974).
- [23] G. Shi and J. H. Seinfeld, *J. Chem. Phys.* **93**, 9033 (1990).
- [24] P. Demo, Z. Kožíšek, and R. Šášik, *Phys. Rev. E* **59**, 5124 (1999); **60**, 4995 (1999).
- [25] B. E. Wyslouzil and G. Wilemski, *J. Chem. Phys.* **105**, 1090 (1996).