

Analytical approach to time lag in binary nucleation

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We present an analytical formula for the time required to establish steady state in a nucleating binary system. To test our solution, we evaluate the time lag for a range of activities of both components at the vapor-liquid transition, and show that our result is in much better agreement with a purely numerical simulation than other available analytical formulas, which overestimate the time lag by factors of from 2 to 200.

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I. INTRODUCTION

For theoretical modeling of nucleation (and, in general, any time-dependent phenomenon) it is often adequate to focus attention only on the steady-state behavior of the system. This, indeed, may be acceptable if the time needed to reach the steady state is negligible in comparison with the time scale of the experiment.

On the other hand, when the time needed to reach the steady state is long (as it is, for instance, for nucleation in glassy-forming melts) or in experiments with very short time scales (e.g., nozzle expansion or shock tubes—see Wyslouzil *et al.* [1]), transient effects may become important and, *ipso facto*, are responsible for the instantaneous properties of the system.

Other recent examples of transient behavior—serving here merely as motivation—completely determining the outcome of an experiment include atomic force microscopy of complex oxide nucleation on a substrate (see Ref. [2]), time-resolved neutron scattering spectroscopy of early stages of nucleation in a polymer mixture (see Ref. [3]), and nucleation of the superconducting phase in indium spheres probed with gamma rays (Meagher *et al.* [4]). Likewise, the analysis of initial stages of Bose-Einstein condensation (see Stoof [5]) also belongs to the case under consideration. Quite generally, it may be expected that the importance of an accurate description of transient behavior in many areas of physics and chemistry will grow further with the refinement of experimental techniques.

The criterion of applicability of the steady-state approach may be naturally quantified in terms of the so-called time lag (time delay) measuring the period during which transient effects decay. In other words, when this time has elapsed, the characteristics of a nucleating system (distribution of clusters, flux density, etc.) become time independent. Such a state corresponds to either the equilibrium state under given conditions, or to a nonequilibrium steady state when the system is attached to a large reservoir maintaining invariability of the density flux (details may be found, e.g., in Refs. [6,7]).

In this paper we calculate the typical time in which flux density in a nucleating binary system approaches the stationary value. Previous workers (see, e.g., Refs. [7–9]) have considered time lags in single-component systems. For binary nucleation there have been derived, *de facto*, only two appli-

cable analytical formulas for the time lag.

Wilemski [10] reduced the problem to an equation describing quasi-single-component nucleation by neglecting the off-saddle-point flux component. Without direct solution of this equation he obtained an approximate expression for the time lag at the saddle point (see also Refs. [10–12]),

$$\tau_w = \frac{3n_C}{2D_C \ln \mathcal{S}_C} \left(\gamma_E + \ln \frac{\Delta G_C}{3} \right), \quad (1)$$

where $n_C = (n_A^C + n_B^C)$ represents the critical cluster consisting of n_A^C (n_B^C) monomers of A (B) component and $\gamma_E = 0.5772$ is Euler's constant. The effective critical supersaturation \mathcal{S}_C can be expressed as $\ln \mathcal{S}_C = x_A^C \ln \mathcal{S}_A + x_B^C \ln \mathcal{S}_B$ ($x_i^C = n_i^C/n_C$ is the mole fraction of the i th component; $\mathcal{S}_i = P_i/P_i^{\text{eq}}$, where P_i corresponds to the pressure of the i th constituent in the gas and P_i^{eq} is the equilibrium vapor pressure over bulk solution, $i=A, B$ —see also Wilemski [10]). ΔG_C corresponds to the Gibbs energy (in $k_B T$ units) required to form a critical cluster from the gaseous phase. Finally, the average impingement rate D_C may be obtained as a combination of the appropriate forward rate coefficients (for details, see Refs. [10] and [11]).

The other formula for time lag in binary nucleating system was derived by Shi and Seinfeld [13]. They applied singular perturbation analysis (for detailed information about this method see Shi, Seinfeld, and Okuyama [8]) to solve the time-dependent nucleation equation within the boundary (transition) layer existing in the vicinity of the saddle point. (It is assumed that the number density of clusters within this critical region is far from equilibrium, while outside of this layer the clusters distribution corresponds to equilibrium of individual monomer concentrations.) Using Laplace transformation, they obtained the effective time lag in a quite general binary system in the form

$$\tau_s = \frac{\tau_0}{2} [\gamma_E + 2\lambda_s + E_1(e^{2\lambda_s})], \quad (2)$$

where $E_1(x)$ is the exponential integral, and τ_0 is the typical time scale characterized by the collision frequency between monomers and critical cluster. (Expressions both for τ_0 and

also for λ_S are too complicated to present them here and the interested reader is referred to Shi and Seinfeld [13] for details.)

In the following we have used the definition for the time delay for binary systems previously introduced by Wyslouzil and Wilemski [11]. (By analogy with the single component system they defined the time delay in terms of the saddle point flux.) We also show that our result is in much better agreement with numerical simulations than formulas (1) and (2).

II. MODEL AND SOLUTION

Consider the nucleation equation expressing the formation of clusters within the binary mother phase:

$$\frac{\partial F}{\partial t} = -\frac{\partial J_A}{\partial n_A} - \frac{\partial J_B}{\partial n_B}, \quad (3)$$

where $F(n_A, n_B, t)$ represents the distribution function of clusters consisting of $n_A(n_B)$ monomers of $A(B)$ species, and the components of the cluster flux density are defined as

$$J_A = -\alpha_A F_0 \frac{\partial y}{\partial n_A}, \quad (4a)$$

$$J_B = -\alpha_B F_0 \frac{\partial y}{\partial n_B}. \quad (4b)$$

Here, $\alpha_A(n_A, n_B)[\alpha_B(n_A, n_B)]$ denotes the probability density that the monomer $A(B)$ joins to a cluster of the composition $n = (n_A + n_B)$, and $y(n_A, n_B, t) \equiv F(n_A, n_B, t)/F_0(n_A, n_B)$ stands for a dimensionless distribution function normalized to the equilibrium canonical distribution $F_0(n_A, n_B)$ given by

$$F_0 = N \exp(-\beta \Delta G). \quad (4c)$$

Above, $\beta = 1/k_B T$, N is the total monomer number concentration (assumed to be a constant), and $\Delta G(n_A, n_B)$ denotes the Gibbs free energy needed to create a cluster of composition $n = (n_A + n_B)$ from the original phase. Next we assume that the binary nucleation starts from the monomers ($n_A = 1, n_B = 0$) or ($n_A = 0, n_B = 1$) of the equilibrium distribution and that the formation of extremely large clusters is practically excluded.

If the distribution function is known, the number density of critical (hence, growth capable) clusters formed during a certain time of observation can be determined in terms of the integrated flux \mathcal{P} at the saddle point as follows:

$$\mathcal{P} = \int_0^t J_C dt' = \int_0^t (J_A^C + J_B^C) dt'. \quad (5)$$

Time lag is then defined from the linear dependency of \mathcal{P} on time. (It can be readily proved that this definition corresponds to that of Wyslouzil and Wilemski [11].)

The problem is that no explicit analytical solution of the Fokker-Planck-like equation (3) is available. Therefore, various approximations are made to obtain approximate expressions for the distribution function. Since for our further purposes the solution of Eq. (3) is required only in the vicinity

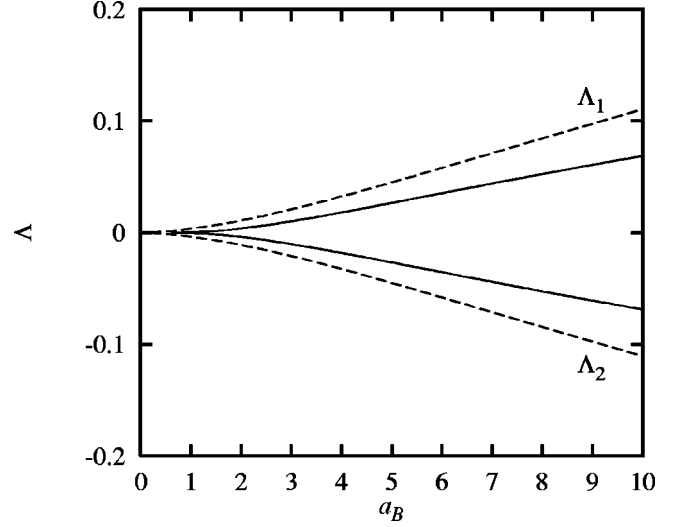


FIG. 1. Eigenvalues $\Lambda_{1,2}$ vs activity a_B for $a_A=0.5$ (full lines) and $a_A=2$ (dashed lines) computed from the relationships (6), (7), and (15a). Input parameters: $T=260$ K, $\sigma=2.5 \times 10^{-2}$ Jm $^{-2}$, and $\gamma=1.1 \times 10^{-18}$ m 2 .

of the saddle point $n_C = (n_A^C + n_B^C)$ —as follows from the definition (5) of the integrated flux—we use approximations for the forward rate coefficients, which enter the Gibbs free energy, without further specification of their explicit forms. First, we replace the rate coefficients by their values at n_C : $\alpha_A(n_A, n_B) \approx \alpha_A^C(n_A^C, n_B^C)$ and $\alpha_B(n_A, n_B) \approx \alpha_B^C(n_A^C, n_B^C)$. Second, we expand $\Delta G(n_A, n_B)$ around the saddle point to second order, and transform the resulting quadratic form to its canonical form. Consider matrix

$$\mathbf{G} = \begin{pmatrix} G_{AA} & G_{AB} \\ G_{BA} & G_{BB} \end{pmatrix}, \quad (6)$$

where $G_{ij} = \beta \sqrt{B_i B_j} (\partial^2 \Delta G / \partial n_i \partial n_j)_C$ and $B_i = \alpha_i^C / (\alpha_A^C + \alpha_B^C)$, $i, j = A, B$. The eigenvalues Λ of \mathbf{G} are found to be

$$\Lambda_{1,2} = \frac{1}{2} \text{Tr} \mathbf{G} \pm \frac{1}{2} \sqrt{(\text{Tr} \mathbf{G})^2 - 4 \det \mathbf{G}}. \quad (7)$$

As we know, ΔG exhibits a saddle point behavior. Therefore, the eigenvalues $\Lambda_{1,2}$ have to be real and of opposite sign; let $\Lambda_1 > 0$ and $\Lambda_2 < 0$ (see Fig. 1). Since the inverse values of $\Lambda_{1,2}$ are closely connected with the set of relaxation times for the nucleation process, the only physically meaningful solution requires $\Lambda \equiv \Lambda_1 > 0$. (Otherwise the solution becomes unstable and strongly divergent under small perturbation.) The components of the eigenvector $\mathbf{e} = [e_A, e_B]$ of the matrix \mathbf{G} corresponding to the eigenvalue Λ may be expressed as

$$[e_A, e_B] = \frac{1}{\sqrt{[(\Lambda - G_{BB})/G_{AB}]^2 + 1}} \left[\left(\frac{\Lambda - G_{BB}}{G_{AB}} \right), 1 \right]. \quad (8a)$$

Then, finally, to transform the system (3,4) to an equation of a solvable form, we apply the mapping

$$x = (\mathbf{e}, \mathbf{z}) \exp(\Lambda \tau) - x_{\min}, \quad (8b)$$

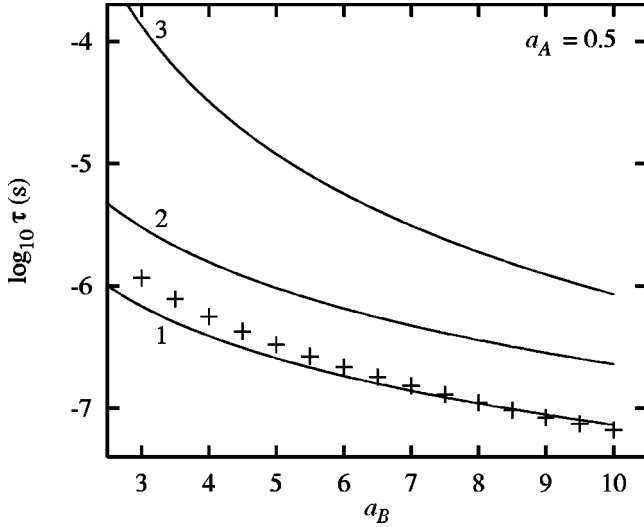


FIG. 2. Decimal logarithm of the time lag τ_D as a function of the activity a_B for $a_A=0.5$. Crosses, numerical calculation; 1, our analytical formula (12); 2, result of Shi and Seinfeld [expression (2)]; 3, time lag after Wilemski [relationship (1)]. Input parameters: $T=260$ K, $\sigma=2.5 \times 10^{-2}$ Jm $^{-2}$, $\gamma=1.1 \times 10^{-18}$ m 2 , $P_A=400$ Pa, $P_B=150$ Pa, $m_A=6.6 \times 10^{-26}$ kg, and $m_B=9.9 \times 10^{-26}$ kg.

where (\mathbf{e}, \mathbf{z}) denotes the scalar product of the orthonormalized eigenvector \mathbf{e} and the size vector $\mathbf{z}=[(n_A - n_A^C)/\sqrt{B_A}, (n_B - n_B^C)/\sqrt{B_B}]$, $\tau=(\alpha_A^C + \alpha_B^C)t$ is the dimensionless time, and $x_{\min}=-((n_A^C e_A/\sqrt{B_A} + n_B^C e_B/\sqrt{B_B}))$. One obtains a simple partial differential equation

$$\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} \exp(2\Lambda \tau), \quad (9)$$

where $\tau \geq 0$ and from the initial condition we obtain $0 \leq x \leq (e_A/\sqrt{B_A} + e_B/\sqrt{B_B})$.

This classical Cauchy problem may be reformulated in the space of generalized functions to obtain a generalized solution in the form of the following convolutory products (for details, see, e.g. Vladimirov [14]):

$$Y = \mathcal{G} * \delta(\tau) + \left(\frac{2\Lambda x}{\exp(2\Lambda \tau) - 1} \right) \mathcal{G} * \exp(2\Lambda \tau) \delta(x), \quad (10)$$

where δ denotes the appropriate Dirac distribution, $Y(x, \tau)$ is the continuation of $y(x, \tau)$ onto interval $(-\infty, 0)$, and

$$\mathcal{G}(x, \tau) = \sqrt{\frac{\Lambda}{2\pi[\exp(2\Lambda \tau) - 1]}} \frac{\exp(-\Lambda x^2)}{2[\exp(2\Lambda \tau) - 1]} \quad (11)$$

is the Green function related to Eq. (9).

Substituting these convolutory integrals into definitions (4a) and (4b) and using relationship (5), we determine the time lag to be

$$\tau_D = \frac{2\gamma_E + 2 \ln(fg) + E_1(f^2) + E_1(g^2)}{4\Lambda(\alpha_A^C + \alpha_B^C)}. \quad (12)$$

This is our final result.

Here

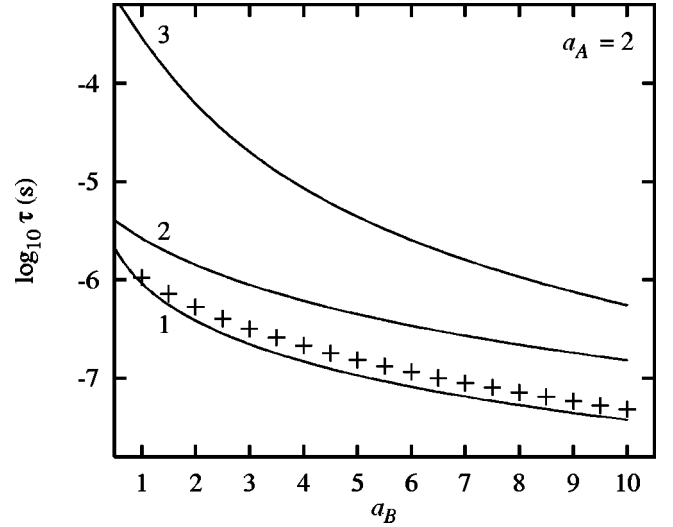


FIG. 3. Decimal logarithm of the time lag τ_D as a function of the activity a_B for $a_A=2$. Crosses, numerical calculation; 1, our analytical formula (12); 2, result of Shi and Seinfeld [expression (2)]; 3, time lag after Wilemski [relationship (1)]. Input parameters: $T=260$ K, $\sigma=2.5 \times 10^{-2}$ Jm $^{-2}$, $\gamma=1.1 \times 10^{-18}$ m 2 , $P_A=400$ Pa, $P_B=150$ Pa, $m_A=6.6 \times 10^{-26}$ kg, and $m_B=9.9 \times 10^{-26}$ kg.

$$f = \sqrt{\frac{\Lambda}{2}} \left(\frac{(n_A^C + 1)e_A}{\sqrt{B_A}} + \frac{(n_B^C + 1)e_B}{\sqrt{B_B}} \right) \quad (13)$$

and

$$g = \sqrt{\frac{\Lambda}{2}} \left(\frac{(n_A^C - 1)e_A}{\sqrt{B_A}} + \frac{(n_B^C - 1)e_B}{\sqrt{B_B}} \right). \quad (14)$$

III. APPLICATION

Note that time lag (12) depends on two complementary factors: static (characterizing the properties of the nucleating system itself via metrics of the Gibbs free energy surface) and dynamic (through the forward rate coefficients). In order to quantitatively test our result, we have to choose specific forms of α_A^C , α_B^C , and ΔG , since formula (12) is quite general without any specification of these quantities. For this purpose consider the condensation of a binary mixture of ideal gases. In this simplest case (and in capillarity approximation—see Wyslouzil and Wilemski [15]) we have

$$\Delta G = -(n_A/\beta) \ln \left(\frac{a_A(n_A + n_B)}{n_A} \right) - (n_B/\beta) \ln \left(\frac{a_B(n_A + n_B)}{n_B} \right) + \gamma \sigma (n_A + n_B)^{2/3}. \quad (15a)$$

The forward rates are chosen to be

$$\alpha_i^C = \frac{P_i}{\sqrt{2\pi m_i/\beta}} \gamma (n_A^C + n_B^C)^{2/3}, \quad (15b)$$

where a_i , P_i , and m_i ($i=A, B$) represent, respectively, the activity, partial pressure, and the mass of the i th component, σ is the interfacial energy (assumed to be constant in this

simplest model), and γ denotes the geometrical factor connected with the surface S_n of the n -sized cluster by $S_n = \gamma(n_A + n_B)^{2/3}$.

The above relations, with the same input parameters, are used for all three formulas (1), (2), and (12) in order to compare them with the purely numerical calculations. Kinetic equation (3) has been solved numerically in a dimensionless form (with F being normalized to the equilibrium distribution F_0) using the standard Runge-Kutta-Fehlberg method with automatic estimation of local error and step size adjustment (see Kožíšek and Demo [16] and references therein). The accuracy of the numerical solution is 1% or better.

Dependence of the time lag on the activity of the B component (for $a_A = 0.5$ and 2) is shown in Figs. 2 and 3. As may be seen, previous analytical predictions overestimate the time lag by factors ranging from 2 [see Eq. (2)] to 200 [for expression (1)]. It has to be pointed out, however, that al-

though our approach and the method applied by Shi and Seinfeld [13] are different, the obtained dependencies of the time lag on activities are very similar.

Because the typical time scale for vapor-liquid transitions is about 10^{-6} s (of course, this value depends on the conditions imposed on the nucleating system), such a difference may play an essential role in the planning of experiments with short time scales.

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- [1] B.E. Wyslouzil, J.L. Cheung, G. Wilemski, and R. Strey, *Phys. Rev. Lett.* **79**, 431 (1997).
- [2] V.C. Matijasevic, B. Ilge, B. Stäuble-Pümpin, G. Rietveld, F. Tuinstra, and J.E. Mooij, *Phys. Rev. Lett.* **76**, 4765 (1996).
- [3] N.P. Balsara, C. Lin, and B. Hammouda, *Phys. Rev. Lett.* **77**, 3847 (1996).
- [4] G. Meagher, D. DiSanto, A. Kotlicki, G. Eska, and B.G. Turrell, *Phys. Rev. Lett.* **79**, 285 (1997).
- [5] H.T.C. Stoof, *Phys. Rev. Lett.* **78**, 768 (1997).
- [6] K.F. Kelton, A.L. Greer, and C.V. Thompson, *J. Chem. Phys.* **79**, 6261 (1983).
- [7] P. Demo and Z. Kožíšek, *Philos. Mag. B* **70**, 49 (1994).
- [8] G. Shi, J.H. Seinfeld, and K. Okuyama, *Phys. Rev. A* **41**, 2101 (1990).
- [9] P. Demo and Z. Kožíšek, *Phys. Rev. B* **48**, 3620 (1993).
- [10] G. Wilemski, *J. Chem. Phys.* **62**, 3772 (1975).
- [11] B.E. Wyslouzil and G. Wilemski, *J. Chem. Phys.* **105**, 1090 (1996).
- [12] V.A. Shneidman and M.C. Weinberg, *J. Chem. Phys.* **97**, 3621 (1992).
- [13] G. Shi and J.H. Seinfeld, *J. Chem. Phys.* **93**, 9033 (1990).
- [14] V. S. Vladimirov, *Generalized Functions in Mathematical Physics* (Mir, Moscow, 1979).
- [15] B.E. Wyslouzil and G. Wilemski, *J. Chem. Phys.* **103**, 1137 (1995).
- [16] Z. Kožíšek and P. Demo, *J. Cryst. Growth* **132**, 491 (1993).