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Binary nucleation kinetics. IV. Directional properties and cluster concentrations at the saddle point

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Using a new approach, Stauffer's expression for the rate of steady state binary nucleation and Trinkaus's expression for the steady state cluster concentrations f are derived directly from the diffusion equation that governs the evolution of f in composition space. The behavior of Φ ($\equiv f/N$, where N is the equilibrium cluster concentration) is explored since this function provides a characterization of the nucleating binary system that, to lowest order, is independent of the actual composition of the mother phase. The angle ω that describes the direction of $\nabla\Phi$ at the saddle point differs, in general, from the angle ϕ found by Stauffer for the direction of the nucleation current at the saddle point. These two angles are related by the formula: $\tan \phi = r \tan \omega$, where r is the ratio of impingement frequencies defined by Stauffer. In general, at the saddle point, $\nabla\Phi$ also fails to lie in the direction of steepest descent on the free energy surface. © 1999 American Institute of Physics. [S0021-9606(99)50613-2]

I. INTRODUCTION

Recently, Wyslouzil and Wilemski^{1,2} published the results of extensive numerical studies of binary nucleation kinetics for six different systems over a reasonable range of nucleation rates. The primary quantities calculated in this work were the time-dependent nonequilibrium concentrations $f(n_1, n_2, t)$ of clusters of composition (n_1, n_2) , where n_i is the number of molecules of species i in the cluster. They found that their numerical results simplified considerably for all the binary systems studied when the $f(n_1, n_2, t)$ were normalized by the equilibrium cluster concentrations $N(n_1, n_2)$. The resulting ratios, which they denoted as Φ ($\equiv f/N$), displayed a quasiuniversal behavior that was independent of the monomer concentrations of each species to a very good first approximation. Some of the theoretical framework needed to understand this behavior is implicit in an important and insightful paper by Trinkaus,³ but the direct connections need to be drawn out. Besides the results presented here, detailed considerations may also be found in two other recent papers.^{4,5}

The main goal of this paper is to provide a basis for interpreting the numerical results of Wyslouzil and Wilemski^{2,5} using relatively simple, physically-based mathematics to derive quantitative expressions for Φ and the direction of its gradient at the saddle point. These quantities are significant because contour lines of constant $\Phi(n_1, n_2)$ form a regular pattern when plotted in the two-dimensional (n_1, n_2) cluster composition space. In particular, in the vicinity of the saddle point the contour lines are locally straight and parallel. The angle ω between $\nabla\Phi$ and the n_1 axis is a convenient way to characterize this behavior. As shown elsewhere,⁵ ω is nearly constant and independent of the composition of the mother phase for nucleated phases that form ideal mixtures. For nonideal mixtures, ω varies systemati-

cally with the mother phase composition. Thus, in either case, ω is a useful quantity to understand, and an explicit formula governing its dependence on the physical properties of the system will be developed. Using a different approach, a very recent paper by Li and Nishioka⁴ treats some of the same issues addressed here. In particular, they find the same result for ω that is presented below.

One key result that will be demonstrated is that in cluster composition space (n_1, n_2) the angle ω differs, in general, from both the angle ϕ found by Stauffer⁶ for the direction of the nucleation flux vector \mathbf{J} at the saddle point, and the angle α of Shi and Seinfeld⁷ that characterizes the principal axis transformation devised by Trinkaus. This demonstration also resolves some existing confusion^{7,8} about the roles of ϕ and α in binary nucleation theory. At the saddle point, \mathbf{J} and $\nabla\Phi$ generally point in different directions. In the space of transformed variables (ν_1, ν_2) , introduced by Trinkaus, α plays the role of both ω and ϕ . That is, the transformed gradient of Φ and the transformed nucleation current \mathbf{i} at the saddle point always lie in the same direction defined by α . The same strategy used by Trinkaus to reduce both problems to a single one-dimensional problem has been generalized in more formal treatments of multiparameter,⁹ binary,¹⁰ and multicomponent nucleation.¹¹

The plan of this paper is as follows. In Sec. II, explicit formulas for Φ and ω are derived, and the direction of $\nabla\Phi$ is established. In Sec. III, the expression for \mathbf{J} at the saddle point and the relationship between ω and ϕ are derived. In Sec. IV, Stauffer's expression⁶ for the steady state rate of binary nucleation is rederived starting from an explicit, but general definition of the nucleation rate. This final exercise is undertaken not only to consummate the preceding analysis but also to provide a more transparent derivation than do the elegant, but less physically intuitive treatments published earlier.^{3,7,9-11} Finally, in the Appendix, the connection be-

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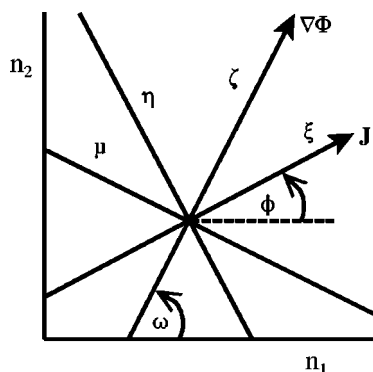


FIG. 1. The ζ - μ and ξ - η coordinate systems used in solving for Φ and \mathbf{J} , respectively. Near the saddle point, $\nabla\Phi$ and \mathbf{J} are parallel to the ζ and ξ axes, respectively. The angles ω and ϕ , determined by Eqs. (24) and (47), are also shown.

tween the present results and those of Trinkaus,³ and Shi and Seinfeld⁷ is established.

II. STEADY STATE SOLUTION FOR Φ

When the cluster composition variables n_1, n_2 are treated as continuous, the fundamental equation governing the evolution of $f(n_1, n_2, t)$ in time t and composition space can be written in the form of a continuity equation,¹²

$$-\frac{\partial f(n_1, n_2, t)}{\partial t} = \nabla \cdot \mathbf{J} = \frac{\partial J_1}{\partial n_1} + \frac{\partial J_2}{\partial n_2}, \quad (1)$$

where the nucleation flux vector \mathbf{J} is defined as

$$\mathbf{J} = J_1 \mathbf{e}_1 + J_2 \mathbf{e}_2, \quad (2)$$

the \mathbf{e}_i are unit vectors in the Cartesian (n_1, n_2) coordinate system, and J_1 and J_2 are the time and composition dependent fluxes given as

$$J_i = -N(n_1, n_2) \Gamma_i N_i \frac{\partial \Phi}{\partial n_i}. \quad (3)$$

In Eq. (3) $\Gamma_i(n_1, n_2)$ is the rate coefficient for adding a monomer of type i to a cluster of composition (n_1, n_2) , and N_i is the monomer number density of species i in the mother phase. To solve Eqs. (1) and (3), we introduce new coordinates ζ and μ that translate the origin to the saddle point (where values are denoted by*) and rotate the n_1 and n_2 axes by an angle ω (see Fig. 1):

$$n_1 - n_1^* = \zeta \cos \omega - \mu \sin \omega, \quad (4)$$

$$n_2 - n_2^* = \zeta \sin \omega + \mu \cos \omega. \quad (5)$$

Since this is an orthogonal transformation, and since at steady state $\partial f / \partial t = 0$, Eq. (1) transforms into

$$0 = \frac{\partial J_\zeta}{\partial \zeta} + \frac{\partial J_\mu}{\partial \mu}, \quad (6)$$

where the new flux components J_ζ and J_μ are defined as

$$J_\zeta = J_1 \cos \omega + J_2 \sin \omega, \quad (7)$$

$$J_\mu = -J_1 \sin \omega + J_2 \cos \omega. \quad (8)$$

Using Eqs. (3), (4), (5), (7), and (8), J_ζ and J_μ can be expressed explicitly as

$$J_\zeta = -N \Sigma(\omega) \frac{\partial \Phi}{\partial \zeta} + N \Delta(\omega) \frac{\partial \Phi}{\partial \mu}, \quad (9)$$

and

$$J_\mu = N \Delta(\omega) \frac{\partial \Phi}{\partial \zeta} - N Y(\omega) \frac{\partial \Phi}{\partial \mu}, \quad (10)$$

where

$$\Sigma(\omega) = R_1 \cos^2 \omega + R_2 \sin^2 \omega, \quad (11)$$

$$\Delta(\omega) = (R_1 - R_2) \cos \omega \sin \omega, \quad (12)$$

$$Y(\omega) = R_1 \sin^2 \omega + R_2 \cos^2 \omega, \quad (13)$$

and where $R_i = \Gamma_i N_i$. To further simplify Eqs. (9) and (10), we impose the condition that $\partial \Phi / \partial \mu = 0$. This condition will shortly be used to determine ω uniquely. More generally, it can be viewed as implicitly defining a curvilinear coordinate system in which Φ is a constant along lines of constant ζ . In general, as μ changes along a constant ζ line, ω will also vary, but in the vicinity of the saddle point it is a very good approximation to hold ω constant. With $\partial \Phi / \partial \mu = 0$, the expressions for J_ζ and J_μ reduce to

$$J_\zeta = -N \Sigma(\omega) \frac{d\Phi}{d\zeta}, \quad (14)$$

and

$$J_\mu = N \Delta(\omega) \frac{d\Phi}{d\zeta}. \quad (15)$$

Note that although $\partial \Phi / \partial \mu = 0$, each of the new flux components is, in general, nonzero in this coordinate system.

Next, we substitute Eqs. (14) and (15) into Eq. (6). In carrying out the required differentiations, R_1 and R_2 are held constant at their saddle point values, R_1^* and R_2^* . Because of this simplification, all of the subsequent results in this paper are generally valid only near the saddle point. The resulting differential equation for Φ is,

$$0 = \Sigma^*(\omega) \frac{d^2 \Phi}{d\zeta^2} + p(\zeta) \frac{d\Phi}{d\zeta}, \quad (16)$$

where

$$p(\zeta) = \Sigma^*(\omega) \left(\frac{\partial \ln N}{\partial \zeta} \right)_\mu - \Delta^*(\omega) \left(\frac{\partial \ln N}{\partial \mu} \right)_\zeta. \quad (17)$$

Because Eq. (16) was obtained by using the condition $\partial \Phi / \partial \mu = 0$, Φ depends only on ζ . Thus, $p(\zeta)$ must also depend only on ζ , and any apparent dependence on μ must be formal. To find an explicit expression for $p(\zeta)$, we exploit the linear dependence of $\ln N$ on the reversible work of cluster formation $W(n_1, n_2)$,

$$kT \ln N = -W + \text{const}, \quad (18)$$

and make the usual quadratic expansion for W in the neighborhood of the saddle point.¹² With $w = W/(kT)$ we have

$$w - w^* = \frac{1}{2} \sum_{i,j} (n_i - n_i^*) w_{ij}^* (n_j - n_j^*), \quad (19)$$

where

$$w_{ij} = \frac{\partial^2 w}{\partial n_i \partial n_j}. \quad (20)$$

With the help of Eqs. (4), (5), (18), and (19), Eq. (17) can be explicitly written as

$$p(\zeta) = \zeta L + \mu M, \quad (21)$$

where

$$\begin{aligned} L = & -\Sigma^*(\omega)[w_{11}^* \cos^2 \omega + w_{12}^* \sin 2\omega + w_{22}^* \sin^2 \omega] \\ & + \Delta^*(\omega)[w_{12}^*(2 \cos^2 \omega - 1) \\ & + (w_{22}^* - w_{11}^*) \sin \omega \cos \omega], \end{aligned} \quad (22)$$

and

$$\begin{aligned} M = & \Delta^*(\omega)[w_{11}^* \sin^2 \omega - w_{12}^* \sin 2\omega + w_{22}^* \cos^2 \omega] \\ & + \Sigma^*(\omega)[w_{12}^*(2 \sin^2 \omega - 1) \\ & + (w_{11}^* - w_{22}^*) \sin \omega \cos \omega]. \end{aligned} \quad (23)$$

The formal μ dependence in Eq. (21) is eliminated by setting M equal to zero. The ensuing equation constitutes a defining relationship for ω , and it yields the following result,

$$\tan \omega = [s + (s^2 + r)^{1/2}] / r, \quad (24)$$

where Stauffer's simplifying notation has been used:

$$r = R_2^* / R_1^*, \quad (25)$$

$$s = (r w_{22}^* - w_{11}^*) / (2 w_{12}^*). \quad (26)$$

Equation (24) is valid for $w_{12}^* < 0$, which should be true for all cases of binary nucleation involving two different chemical species. For other types of phase transformations^{9,13} that are formally describable in terms of binary nucleation, it may be possible that $w_{12}^* > 0$. In these cases, Eq. (24) requires a sign change.¹³

With the μ dependence removed, Eq. (21) reduces to

$$p(\zeta) = \zeta L, \quad (27)$$

and L may be written more simply as

$$\begin{aligned} L = & -(R_1^* w_{11}^* \cos^2 \omega + (R_1^* + R_2^*) w_{12}^* \cos \omega \sin \omega \\ & + R_2^* w_{22}^* \sin^2 \omega). \end{aligned} \quad (28)$$

Equation (27) may be used to recast Eq. (16) as

$$\frac{d^2 \Phi}{d\zeta^2} = -\zeta \Lambda \frac{d\Phi}{d\zeta}, \quad (29)$$

where Λ is a positive constant,

$$\Lambda = L / \Sigma^*(\omega). \quad (30)$$

With the usual boundary conditions

$$\Phi(\zeta) = 1, \quad \zeta \rightarrow -\infty, \quad (31)$$

$$\Phi = 0, \quad \zeta \rightarrow \infty, \quad (32)$$

which correspond to the smallest clusters being present at their equilibrium concentrations and the largest being absent, Eq. (29) admits the following solution that will later be shown to be equivalent to Trinkaus's:

$$\frac{d\Phi}{d\zeta} = -\left(\frac{\Lambda}{2\pi}\right)^{1/2} \exp\left(-\frac{1}{2}\Lambda\zeta^2\right), \quad (33)$$

$$\Phi(\zeta) = \frac{1}{2} \operatorname{erfc}(\sqrt{\Lambda/2}\zeta). \quad (34)$$

As a minor sidelight, note that at the saddle point ($\zeta=0$) Eq. (34) predicts that the steady state critical nucleus concentration is one-half of the equilibrium value, just as for the case of unary nucleation¹⁴ and in agreement with numerical results.^{2,5} The dependence of Φ and $d\Phi/d\zeta$ on n_1 and n_2 may be found simply by inverting Eqs. (4) and (5) to obtain

$$\zeta = (n_1 - n_1^*) \cos \omega + (n_2 - n_2^*) \sin \omega, \quad (35)$$

which may then be substituted into Eqs. (33) and (34). Similarly, the nucleation flux components J_1 and J_2 may be evaluated in the neighborhood of the saddle point by first inverting Eqs. (7) and (8) followed by using Eqs. (14), (15), and (33) to determine J_ζ and J_μ .

The direction of $\nabla\Phi$ near the saddle point is easy to establish since Φ depends only on ζ . Use of the chain rule yields

$$\nabla\Phi = \left[\left(\frac{\partial\zeta}{\partial n_1} \right)_{n_2} \mathbf{e}_1 + \left(\frac{\partial\zeta}{\partial n_2} \right)_{n_1} \mathbf{e}_2 \right] \frac{d\Phi}{d\zeta}, \quad (36)$$

which can be simplified using Eq. (35) to read

$$\nabla\Phi = \mathbf{e}_\zeta \frac{d\Phi}{d\zeta}, \quad (37)$$

where \mathbf{e}_ζ is the unit vector in the (ζ, μ) coordinate system that makes an angle ω with the n_1 axis

$$\mathbf{e}_\zeta = \cos \omega \mathbf{e}_1 + \sin \omega \mathbf{e}_2. \quad (38)$$

III. MAGNITUDE AND DIRECTION OF NUCLEATION FLUX AT THE SADDLE POINT

We now return to Eqs. (1) and (3) and, like Stauffer,⁶ introduce two new coordinates ξ and η , analogous to those of the preceding section, that translate the origin to the saddle point and rotate the n_1 and n_2 axes by an angle ϕ (see Fig. 1):

$$n_1 - n_1^* = \xi \cos \phi - \eta \sin \phi, \quad (39)$$

$$n_2 - n_2^* = \xi \sin \phi + \eta \cos \phi. \quad (40)$$

In the new coordinate system, the flux components are defined as

$$J_\xi = J_1 \cos \phi + J_2 \sin \phi, \quad (41)$$

$$J_\eta = -J_1 \sin \phi + J_2 \cos \phi. \quad (42)$$

The new flux components, J_ξ and J_η , satisfy equations analogous to Eqs. (9) and (10) with $(\phi, \xi, \text{ and } \eta)$ replacing $(\omega, \zeta, \text{ and } \mu)$, respectively. By means of the chain rule, these equations can be written as

$$J_{\xi} = N \left[\Delta(\phi) \left(\frac{\partial \zeta}{\partial \eta} \right)_{\xi} - \Sigma(\phi) \left(\frac{\partial \zeta}{\partial \xi} \right)_{\eta} \right] \frac{d\Phi}{d\zeta}, \quad (43)$$

$$J_{\eta} = N \left[\Delta(\phi) \left(\frac{\partial \zeta}{\partial \xi} \right)_{\eta} - Y(\phi) \left(\frac{\partial \zeta}{\partial \eta} \right)_{\xi} \right] \frac{d\Phi}{d\zeta}, \quad (44)$$

where it follows from Eqs. (4), (5), (39), and (40) that

$$\left(\frac{\partial \zeta}{\partial \xi} \right)_{\eta} = \cos \phi \cos \omega + \sin \phi \sin \omega, \quad (45)$$

and

$$\left(\frac{\partial \zeta}{\partial \eta} \right)_{\xi} = \cos \phi \sin \omega - \sin \phi \cos \omega. \quad (46)$$

The functions Σ , Δ , and Y are defined by Eqs. (11), (12), and (13). If ϕ is properly chosen, J_{η} will equal zero at the saddle point, leaving J_{ξ} equal to the total nucleation current there. To force $J_{\eta} = 0$, we set the coefficient of $d\Phi/d\zeta$ in Eq. (44) equal to zero. This defines a unique relation between ω and ϕ that can be simplified to read

$$\tan \phi = r \tan \omega, \quad (47)$$

where r has previously been defined in Eq. (25). With Eq. (24), Eq. (47) naturally reduces to Stauffer's⁶ result for $\tan \phi$. From Eq. (47), it is clear that the angles ϕ and ω are equal only when $r = 1$, i.e., when the monomer impingement frequencies R_1^* and R_2^* are equal. In this special case, ϕ and ω are identical to the angle¹² defining the direction of steepest descent. Using Eqs. (45), (46), and (47), we can now simplify Eq. (43) to read

$$J_{\xi} = -NR_1^* R_2^* [\sigma(\phi)]^{-1} \frac{d\Phi}{d\zeta}, \quad (48)$$

where

$$\sigma(\phi) = [(R_1^*)^2 \sin^2 \phi + (R_2^*)^2 \cos^2 \phi]^{1/2}. \quad (49)$$

This result, which renders the saddle point nucleation flux fully calculable, has thus been obtained by an explicit method as an alternative to Stauffer's⁶ more heuristic approach. At this point the total nucleation rate could be obtained simply by integrating Eq. (48) with respect to η on a path through the saddle point, but a somewhat more general approach will be followed in the next section.

The direction of \mathbf{J} in (n_1, n_2) space is easy to establish. Since $J_{\eta} = 0$, it follows from Eqs. (2), (41), and (42) that

$$\mathbf{J} = J_{\xi} \mathbf{e}_{\xi}, \quad (50)$$

where \mathbf{e}_{ξ} is the unit vector in the (ξ, η) coordinate system that makes an angle ϕ with the n_1 axis

$$\mathbf{e}_{\xi} = \cos \phi \mathbf{e}_1 + \sin \phi \mathbf{e}_2. \quad (51)$$

IV. STEADY STATE SADDLE POINT NUCLEATION RATE

The goal of this section is to explicitly derive the steady state rate of binary nucleation while avoiding Stauffer's⁶ original intuitive and heuristic arguments. This has already been done several times,^{3,7,10,11} but except for Wu's very

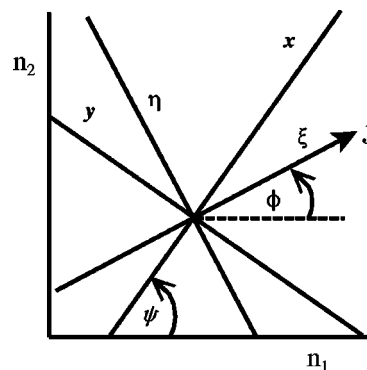


FIG. 2. The x - y coordinate system used in evaluating the total nucleation rate. Any value of the rotation angle ψ in the range, $0 < \psi < \pi/2$, is acceptable.

formal presentation,¹¹ these derivations rely on intuitive or verbal definitions of the nucleation rate that are not so easy to interpret because the initial definition already involves a transformed variable space.

In an effort to be as clear as possible, this derivation will start with an explicit mathematical definition of the rate in (n_1, n_2) space that is systematically evaluated using the results of the preceding sections. As discussed by Temkin and Shevelev,¹⁵ Wu,¹¹ Wyslouzil and Wilemski,¹ the steady state rate of nucleation may be calculated by integrating the normal component of the nucleation flux crossing any line drawn appropriately between the n_1 and n_2 axes in the cluster composition space. Since from analytical theories we generally have detailed knowledge about the nucleation flux only in the vicinity of the saddle point, it makes sense to draw this line through the saddle point. It is also mathematically convenient to make the line straight when only one saddle point is present. As long as it intercepts both positive n_1 and n_2 axes, the orientation of the line is arbitrary, although various special choices have usually been made in the past for convenience.^{3,6,7,12,15} Here, a slightly more general approach will be taken, and the orientation of the line will be described in terms of an angle ψ made by the normal to this line with the n_1 axis, as shown in Fig. 2. The line itself serves as the y axis of a new orthogonal coordinate system centered on the saddle point.

It follows from this discussion that the nucleation rate J may be defined by the two-dimensional integral,

$$J = \int (\mathbf{J} \cdot \mathbf{e}_x) \delta(x) dn_1 dn_2. \quad (52)$$

The integration range includes all physical values of n_1 and n_2 , since the delta function forces the integration to occur only along the new y axis, $x = 0$. The nucleation flux normal to this line is given by the dot product $\mathbf{J} \cdot \mathbf{e}_x$, where \mathbf{e}_x is the unit vector along the new x axis, $\mathbf{e}_x \cdot \mathbf{e}_1 = \cos \psi$. The new coordinates x and y , analogous to those used in the preceding sections, translate the origin to the saddle point and rotate the n_1 and n_2 axes by the angle ψ :

$$n_1 - n_1^* = x \cos \psi - y \sin \psi, \quad (53)$$

$$n_2 - n_2^* = x \sin \psi + y \cos \psi. \quad (54)$$

Since this transformation is orthogonal, its Jacobian is unity, $dn_1 dn_2 = dx dy$, and with Eqs. (50) and (51), Eq. (52) may be written as

$$J = \int J_\xi \delta(x) (\cos \psi \cos \phi + \sin \psi \sin \phi) dx dy. \quad (55)$$

Because of the delta function, the x integration is formally trivial to perform, but the remaining y integral must then be performed with the function J_ξ evaluated on the $x=0$ line. In order to carry this out, we first invert Eqs. (53) and (54) for x and y ,

$$x = (n_1 - n_1^*) \cos \psi + (n_2 - n_2^*) \sin \psi, \quad (56)$$

$$y = -(n_1 - n_1^*) \sin \psi + (n_2 - n_2^*) \cos \psi. \quad (57)$$

Next, after Eqs. (39) and (40) are substituted for n_1 and n_2 in Eqs. (56) and (57), Eq. (56) is set equal to zero to relate ξ and η along the $x=0$ line. It follows from Eq. (57) that

$$\eta = y (\cos \psi \cos \phi + \sin \psi \sin \phi). \quad (58)$$

Thus, along the $x=0$ line, η and y are directly proportional, and Eq. (55) simplifies to

$$J = \int J_\xi \delta(x) dx d\eta. \quad (59)$$

From Eq. (48), J_ξ is a known function of ζ and μ . To transform it into a form suitable for integration, the simplest way to proceed is through the use of an intermediate variable set, ξ_T, η_T , discussed in the Appendix. Using Eqs. (A16) and (A27), Eq. (48) may then be written as

$$J_\xi = N^* R_1^* R_2^* \sqrt{\Lambda / [2 \pi \sigma^2(\phi)]} \exp(-\beta \gamma \eta_T^2 / 2), \quad (60)$$

where $\beta = (kT)^{-1}$ and γ is defined by Eq. (A9). The integral may then be completed by relating η and η_T along the $x=0$ line. To do this, first use Eqs. (A1), (A2), and (A7) to express η_T in terms of n_1 and n_2 . Next use Eqs. (53) and (54) with $x=0$ to obtain η_T in terms of y , and finally replace y in favor of η using Eq. (58) to find

$$\eta_T = \eta / \rho(\phi), \quad (61)$$

where

$$\rho(\phi) = (R_1^* \sin^2 \phi + R_2^* \cos^2 \phi)^{1/2}. \quad (62)$$

Thus, along the $x=0$ line, η and η_T are also directly proportional, and with Eq. (60) for J_ξ and Eq. (A25) for Λ , Eq. (59) further reduces to an explicit version of Trinkaus's³ verbal definition of the nucleation rate,

$$J = N^* \sqrt{R_1^* R_2^* \beta |\lambda| / (2\pi)} \int \exp(-\beta \gamma \eta_T^2 / 2) d\eta_T, \quad (63)$$

where λ is defined by Eq. (A8). Using Eq. (61), J can equivalently be written as an integral over η , as suggested near the end of Sec. III. In either form, the integration now runs along the stable direction through the saddle point. Assuming integration limits¹⁶ of $\pm \infty$, the remaining integral is easily done. The result,

$$J = N^* \sqrt{R_1^* R_2^* |\lambda| / \gamma}, \quad (64)$$

can be put into Trinkaus's form by eliminating γ with the following identity,

$$\beta^2 |\lambda| \gamma = R_1^* R_2^* ((w_{12}^*)^2 - w_{11}^* w_{22}^*). \quad (65)$$

Stauffer's form is obtained by substituting Eq. (65) into Eq. (64) and rewriting λ as

$$\frac{-\beta \lambda}{R_1^* R_2^*} = \frac{(w_{11}^* \cos^2 \phi + 2w_{12}^* \cos \phi \sin \phi + w_{22}^* \sin^2 \phi)}{R_1^* \sin^2 \phi + R_2^* \cos^2 \phi}, \quad (66)$$

with the help of Eq. (30), (24), (47), (A23), (A24), and (A25).

V. SUMMARY AND DISCUSSION

Two complementary ways have been illustrated to transform the original two-dimensional binary nucleation kinetics equations into effective one-dimensional problems: one for the normalized cluster concentrations Φ and the other for the nucleation flux vector \mathbf{J} . In the normal cluster composition space (n_1, n_2) , the directions of $\nabla \Phi$ and \mathbf{J} at the saddle point are generally different. These directions are, however, not independent. They are specified by the angles ω and ϕ , respectively, that are uniquely related by Eq. (47). As discussed in the Appendix, in the transformed space of Trinkaus's³ scaled variables (ν_1, ν_2) , these two distinct one-dimensional descriptions are merged into one: $\nabla_\nu \Phi$ and the transformed nucleation flux vector \mathbf{i} always lie in the same direction given by the angle α , first introduced, but incorrectly characterized by Shi and Seinfeld.^{7,8} In the special case of equal impingement rates ($r=1$) ω , ϕ , and α are identical, and they define the direction of steepest descent.

Stauffer's⁶ explanation for the direction of \mathbf{J} at the saddle point is still valid: The kinetic effect of different rates of monomer impingement on critical clusters causes the nucleation path to deviate from the path of steepest descent on the free energy surface. Since the Φ are, in essence, non-equilibrium cluster concentrations, they are subject to a kinetic influence similar to that affecting \mathbf{J} , and $\nabla \Phi$ also fails to lie on the path of steepest descent. Moreover, since the components of \mathbf{J} are proportional to the components of $\nabla \Phi$ and since the proportionality coefficients are themselves functions of the impingement rates, it is understandable that the directions of \mathbf{J} and $\nabla \Phi$ will also differ, in general, due to this kinetic effect.

The formula derived here for ω , in Eq. (24), and elsewhere by Li and Nishioka,⁴ provides the explicit dependence of ω on the impingement rates and on the second derivatives of the free energy surface at the saddle point. This formula will be useful for exploring the strikingly simple behavior shown by Φ , and it allows further quantitative testing of analytical binary nucleation theory to be performed. The results of these latter investigations have been reported in a separate publication.⁵

Finally, Stauffer's formula for the steady state rate of binary nucleation has been derived from a clear, physically justifiable definition of the nucleation rate using explicit,

straightforward mathematical techniques that, it is hoped, will be easier to follow than the elegant, but more abstruse approaches used previously.^{3,7,10,11}

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APPENDIX

In this Appendix, the relationship of the present results to those of Trinkaus³ is established. To solve Eq. (1) at steady state, Trinkaus³ introduced new variables ν_1 and ν_2 :

$$n_1 - n_1^* = (R_1^*)^{1/2} \nu_1, \quad (\text{A1})$$

$$n_2 - n_2^* = (R_2^*)^{1/2} \nu_2. \quad (\text{A2})$$

In terms of these scaled variables, the quadratic expansion for W , Eq. (19), takes the form

$$W - W^* = \frac{1}{2} \sum_{i,j} \nu_i \Gamma_{ij}^T \nu_j, \quad (\text{A3})$$

where

$$\beta \Gamma_{ij}^T = (R_i^*)^{1/2} w_{ij}^* (R_j^*)^{1/2}, \quad (\text{A4})$$

$\beta = (kT)^{-1}$, and the superscript T (for Trinkaus) is used to avoid confusion between the matrix elements Γ_{ij}^T and the forward rate coefficients Γ_i used earlier in Eq. (3). The advantage of this approach is that in terms of the principal axes coordinates ξ_T and η_T (again, subscript T for Trinkaus) that diagonalize Eq. (A3), the stationary form of Eq. (1) becomes separable and amenable to direct solution.

Trinkaus's extremely economical presentation left many details implicit, but Shi and Seinfeld⁷ provided explicit results for his principal axis transformation. These are reproduced here in a different notation that is closer to that of Trinkaus. The diagonalized form of Eq. (A3) is

$$W - W^* = (\lambda \xi_T^2 + \gamma \eta_T^2)/2, \quad (\text{A5})$$

where the rotated coordinates for the unstable (ξ_T) and stable (η_T) directions are defined in terms of a rotation angle α in the (ν_1, ν_2) coordinate system (see Fig. 3):

$$\xi_T = \nu_1 \cos \alpha + \nu_2 \sin \alpha, \quad (\text{A6})$$

$$\eta_T = -\nu_1 \sin \alpha + \nu_2 \cos \alpha. \quad (\text{A7})$$

The corresponding negative (λ) and positive (γ) eigenvalues are

$$\lambda = (\Gamma_{11}^T + \Gamma_{22}^T - G)/2, \quad (\text{A8})$$

and

$$\gamma = (\Gamma_{11}^T + \Gamma_{22}^T + G)/2, \quad (\text{A9})$$

where

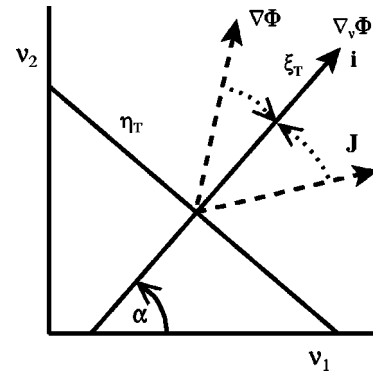


FIG. 3. The ν_1 - ν_2 and ξ_T - η_T coordinate systems introduced by Trinkaus³ to solve for Φ and \mathbf{J} . The transformation of $\nabla\Phi$ and \mathbf{J} into $\nabla_\nu\Phi$ and \mathbf{i} is figuratively illustrated. Near the saddle point $\nabla_\nu\Phi$ and \mathbf{i} are each parallel to the ξ_T axis. The angle α , determined by Eq. (A11), is also shown.

$$G = \sqrt{(\Gamma_{11}^T - \Gamma_{22}^T)^2 + 4(\Gamma_{12}^T)^2}. \quad (\text{A10})$$

Finally, α is determined by the equation

$$\tan \alpha = (\Gamma_{22}^T - \Gamma_{11}^T - G)/(2\Gamma_{12}^T), \quad (\text{A11})$$

which differs from the Shi and Seinfeld⁷ result by the sign of the G term. As discussed by Berezhkovskii and Zitserman¹⁷ and Wyslouzil and Wilemski,¹⁸ the negative sign is needed to ensure the proper orientation at the saddle point when $w_{12}^* < 0$. Using Eqs. (25), (26), and (A4), Eq. (A11) can be put in the form,

$$\tan \alpha = r^{-1/2} [s + (s^2 + r)^{1/2}] = r^{-1/2} \tan \phi, \quad (\text{A12})$$

first noted by Berezhkovskii and Zitserman.¹⁹ It shows clearly that α and ϕ are mathematically distinct quantities contrary to the assertion of Shi and Seinfeld.⁷ It should also be clear that, contrary to another assertion of Shi and Seinfeld, α does not determine the direction of the saddle point nucleation flux with respect to the n_1 axis, since this is done by ϕ . Rather, it is the direction of the transformed nucleation flux \mathbf{i} , defined by Trinkaus, that is determined by α in the (ν_1, ν_2) coordinate system.

This will be clear after examining Trinkaus's results, which can be written in the present notation as

$$\Phi = \frac{1}{2} \operatorname{erfc}(\sqrt{\beta|\lambda|/2}\xi_T), \quad (\text{A13})$$

$$\mathbf{J} = N^* \mathbf{u} \sqrt{\beta|\lambda|/(2\pi)} \exp(-\beta\gamma\eta_T^2/2), \quad (\text{A14})$$

where

$$\mathbf{u} = (R_1^*)^{1/2} \cos \alpha \mathbf{e}_1 + (R_2^*)^{1/2} \sin \alpha \mathbf{e}_2. \quad (\text{A15})$$

Equation (A14) shows explicitly how \mathbf{J} varies with η_T on either side of the saddle point. This expression for \mathbf{J} follows from the definition, Eq. (2), when the flux components J_i are evaluated near the saddle point using Eqs. (3), (A1), (A2), (A5), (A6), and (A13). The identity,

$$N \exp(\beta\lambda \xi_T^2/2) = N^* \exp(-\beta\gamma\eta_T^2/2), \quad (\text{A16})$$

which is valid near the saddle point and follows from Eqs. (18) and (A5), has also been used to simplify Eq. (A14). Trinkaus's transformed nucleation flux vector \mathbf{i} in the (ν_1, ν_2) coordinate system is

$$\mathbf{i} = N^* \mathbf{v} \sqrt{R_1^* R_2^* \beta |\lambda| / (2\pi)} \exp(-\beta \gamma \eta_T^2 / 2), \quad (\text{A17})$$

where

$$\mathbf{v} = \cos \alpha \mathbf{e}_1 + \sin \alpha \mathbf{e}_2, \quad (\text{A18})$$

is the unit vector making an angle α with the ν_1 (or n_1) axis. It is obvious that \mathbf{i} , not \mathbf{J} , makes an angle α with the n_1 axis. The direction of \mathbf{J} is not so clear from Eq. (A14), but it may be discerned by using Eq. (A12) to express $\sin \alpha$ and $\cos \alpha$ in terms of ϕ ,

$$\sin \alpha = (R_1^*)^{1/2} \sin \phi / \rho(\phi), \quad (\text{A19})$$

$$\cos \alpha = (R_2^*)^{1/2} \cos \phi / \rho(\phi), \quad (\text{A20})$$

where $\rho(\phi)$ is defined by Eq. (62). With these substitutions, Eq. (A14) simplifies to

$$\mathbf{J} = \mathbf{e}_\xi (\mathbf{i} \cdot \mathbf{v}) / \rho(\phi), \quad (\text{A21})$$

where \mathbf{e}_ξ has previously been defined in Eq. (51). The direction and magnitude of \mathbf{J} are, thus, in accord with the results of Sec. III provided it can be shown that

$$J_\xi = (\mathbf{i} \cdot \mathbf{v}) / \rho(\phi), \quad (\text{A22})$$

is identical to the combination of Eqs. (48) and (33).

To do this, we first consider the quantity Λ in Eq. (33), which is defined by Eqs. (30), (28), and (11). From Eq. (47) it follows that

$$\sin \omega = R_1^* \sin \phi / \sigma(\phi), \quad (\text{A23})$$

$$\cos \omega = R_2^* \cos \phi / \sigma(\phi), \quad (\text{A24})$$

where $\sigma(\phi)$ is defined by Eq. (49). With these relations and with the help of Eqs. (A4), (A11), and (A12), Λ can be rewritten as

$$\Lambda = - \frac{\beta \lambda}{R_1^* R_2^*} \left(\frac{\sigma(\phi)}{\rho(\phi)} \right)^2. \quad (\text{A25})$$

We next need to relate ζ and ξ_T . To do this, combine Eq. (35) with Eqs. (A1), (A2), (A6), and (A7) while using Eqs. (A19), (A20), (A23), and (A24) to simplify the intermediate expression. The final result is

$$\zeta = \xi_T (R_1^* R_2^*)^{1/2} \rho(\phi) / \sigma(\phi). \quad (\text{A26})$$

From Eqs. (A25) and (A26), it thus follows that

$$\Lambda \zeta^2 = -\beta \lambda \xi_T^2, \quad (\text{A27})$$

and the two expressions for Φ , Eqs. (34) and (A13), are identical. To complete this exercise, combine Eqs. (33) and (48) with Eqs. (A25) and (A27), and use Eq. (A16) to obtain

$$J_\xi = N^* \sqrt{R_1^* R_2^* \beta |\lambda| / (2\pi \rho^2(\phi))} \exp(-\beta \gamma \eta_T^2 / 2), \quad (\text{A28})$$

which agrees with Eq. (A22).

Our last task in this section is to establish the direction of $\nabla_\nu \Phi$ near the saddle point. Since Φ depends only on ξ_T , use of the chain rule yields

$$\nabla_\nu \Phi = \left[\left(\frac{\partial \xi_T}{\partial \nu_1} \right)_{\nu_2} \mathbf{e}_1 + \left(\frac{\partial \xi_T}{\partial \nu_2} \right)_{\nu_1} \mathbf{e}_2 \right] \frac{\partial \Phi}{\partial \xi_T}, \quad (\text{A29})$$

which can be simplified using Eq. (A6) to read

$$\nabla_\nu \Phi = \mathbf{v} \frac{\partial \Phi}{\partial \xi_T}. \quad (\text{A30})$$

Thus, in the (ν_1, ν_2) coordinate system, depicted in Fig. 3, both \mathbf{i} and $\nabla_\nu \Phi$ point in the same direction as \mathbf{v} , and the angle α plays both of the roles held by the angles ω and ϕ in the (n_1, n_2) coordinate system.

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¹⁷The discussion follows Eq. (10) of Ref. 13. Similar considerations apply to Eq. (A11) of this paper and to Eq. (13) of Ref. 13, although the latter equation unfortunately contains a typographical sign error.

¹⁸See Ref. 42 of Ref. 2.

¹⁹Ref. 13 uses ψ instead of α for the angle in question.