

## Genuine saddle point and nucleation potential for binary systems

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A generalized nucleation potential is constructed for binary systems. The potential consists of the reversible work of cluster formation plus additional terms arising from various kinetic effects. We show that the major nucleation flux passes through the saddle point (termed the genuine saddle point) of this generalized nucleation potential. The generalized nucleation potential reduces to the kinetic potential of a unary system when one component vanishes. The genuine saddle point concept provides a convenient way to identify systems and conditions for which the ridge crossing phenomenon occurs. Our theory agrees approximately with exact numerical results.

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The problem of determining nucleation flux trajectories in systems with multiple order parameters is quite old and goes back, at least, to the early work of Reiss [1] on binary nucleation. He proposed the idea that the major nucleation flux passes through a saddle point on  $W^{rev}$ , the surface of reversible work for cluster formation. He then equated the rate of nucleation of the new phase with the size of this flux. Subsequently, Langer [2,3] developed a very general treatment of nucleation rates in terms of the phase space probability flux flowing across a saddle point on the multidimensional energy surface of the system. This flux represents the rate at which metastable systems pass into a state of greater stability. The applicability of the saddle point concept has been demonstrated to be of great value in a wide variety of physical and chemical systems (see, e.g., Ref. [4] and references therein). Recently, the problem of the saddle point location was discussed in connection with the nucleation kinetics during a martensitic transformation [5] and also in the context of the kinetic pathway problem in the segregation process [6,7]. However, at present our ability to relate the pathways of the nucleation flux to the saddle point location in a specific multicomponent system is still incomplete. In this Rapid Communication we offer an answer to this question for the case of binary nucleation.

In his pioneering study of the kinetics of binary nucleation, Reiss [1] assumed that the major nucleation flux follows the path of steepest descent through the saddle point of  $W^{rev}$ . [We call it the thermodynamic saddle point (TSP) to distinguish it from saddle points on other surfaces.] This assumption was followed by other authors [8–11], but Stauffer [12] provided an important clarification by showing that the flux direction at the TSP depends on the monomer impingement rates and, in general, does not follow the path of steepest descent. Following the initial suggestions of Stauffer and Kiang [13] and Stauffer [12] that in certain cases the major nucleation flux *bypasses* the TSP, Trinkaus [14] developed an extensive theory for this phenomenon, which is referred to as ridge crossing of the  $W^{rev}$ . Recent numerical results have demonstrated quite clearly that ridge crossing can occur [15–17]. Although this subject has continued to receive attention [18–21], at present it is still not easy to determine in

which physical systems ridge crossing is likely to occur; nor is it simple to find the location of the major nucleation flux when it does occur.

Nucleation is fundamentally a kinetic process in which an energetic barrier, the nucleation barrier, must be surmounted. The nucleation barrier plays a role similar to the activation energy in conventional chemical kinetics. For unary nucleation, the relevant nucleation barrier is the kinetic potential  $W^K$  that consists of the reversible work of cluster formation and the so-called kinetic term [22,23]. It has been shown that the kinetic term plays a very important role in predicting the transient nucleation kinetics for the case of a low thermodynamic barrier [24]. For binary systems, there should also exist a relevant potential with a saddle point through which the major nucleation flux passes. The identification of this potential is of both practical and theoretical interest in binary nucleation theory. Once the saddle point is located, the pathway of the major nucleation flux can also be determined, and we can use the saddle point approximation to get the nucleation rate. Obviously, this potential will, in general, not coincide with the reversible work, because the latter depends only on thermodynamic parameters. However, it was found recently that the relevant potential is not equivalent to the kinetic potential  $W^K$  either, since the major nucleation flux bypasses the saddle point of  $W^K$  in some cases [25]. Thus, the simple extension of the kinetic potential from a unary system to a binary one is ineffective. Recently, Li *et al.* [26] proposed a generalized kinetic potential that governs the magnitude of the nucleation flux. Although the generalized kinetic potential contains sufficient information to determine the pathway of the major nucleation flux, it does not give an explicit nucleation barrier, for technical reasons that are explained below, and it is also difficult to work with. Here, we propose a potential for the nucleation barrier that determines the nucleation pathway for binary systems.

We consider the process of homogeneous nucleation of liquid clusters in a metastable binary vapor of condensible species  $A$  and  $B$  at a temperature  $T$ . The basic equation governing the time dependent cluster concentrations  $f(n_A, n_B, t)$  may be written as [1]

$$\frac{\partial f(n_A, n_B, t)}{\partial t} = - \frac{\partial J_A(n_A, n_B, t)}{\partial n_A} - \frac{\partial J_B(n_A, n_B, t)}{\partial n_B}, \quad (1)$$

where  $n_i$  ( $i=A,B$ ) denotes the number of  $i$  molecules in a cluster. The components  $J_A(n_A, n_B, t)$  and  $J_B(n_A, n_B, t)$  of the nucleation flux  $\mathbf{J}=(J_A, J_B)$  are given by [1]

$$J_A(n_A, n_B, t) = -F(n_A, n_B)K_A^+(n_A, n_B) \times \frac{\partial}{\partial n_A} \left( \frac{f(n_A, n_B, t)}{F(n_A, n_B)} \right), \quad (2)$$

$$J_B(n_A, n_B, t) = -F(n_A, n_B)K_B^+(n_A, n_B) \times \frac{\partial}{\partial n_B} \left( \frac{f(n_A, n_B, t)}{F(n_A, n_B)} \right), \quad (3)$$

where  $F(n_A, n_B)$  denotes the metastable equilibrium concentration of clusters specified by  $n_A$  and  $n_B$  and  $K_i^+$  is the impingement rate for species  $i$ . The function  $F(n_A, n_B)$  is given by

$$F(n_A, n_B) = F_0(n_A, n_B) \exp[-W^{rev}(n_A, n_B)/kT], \quad (4)$$

where  $F_0(n_A, n_B)$  denotes a prefactor that may depend on the cluster composition, temperature, or other molecular parameters [27]. Equation (1) represents the conservation of total cluster number density, and it holds when cluster coalescence is negligible. This will usually be the case for the nucleation stage before the growth stage starts.

We employ the force vector field  $\mathbf{V}=(V_A, V_B)$  derived from the potential  $\Phi=f/F$  as  $\mathbf{V}=-\nabla\Phi$ . The direction of  $\mathbf{V}$  in the size space is denoted by an angle  $\theta$  with respect to the  $n_A$  axis, and it is related to the direction  $\phi$  of the nucleation flux by [26]

$$\tan \theta(n_A, n_B, t) = \tan \phi(n_A, n_B, t)/r, \quad (5)$$

where  $r \equiv K_B^+/K_A^+$  is a constant.

Further we introduce time-dependent orthogonal curvilinear coordinates  $\xi$  and  $\eta$ , in which  $\xi$  denotes the lines of flow of the vector field  $\mathbf{V}$  and  $\eta$  the contour lines of constant  $\Phi$  (referred to elsewhere [28,29] as  $\Phi$  lines). The coordinate transformation can be expressed as [30]

$$\delta n_A = h_1 \delta \xi \cos \theta - h_2 \delta \eta \sin \theta, \quad (6)$$

$$\delta n_B = h_1 \delta \xi \sin \theta + h_2 \delta \eta \cos \theta, \quad (7)$$

where  $\delta X$  ( $X=\xi, \eta, n_A, n_B$ ) denotes an infinitesimal difference along  $\mathbf{X}$  axis, and  $h_1$  and  $h_2$  denote the scale factors. By employing Eqs. (6) and (7), we obtain [26]

$$J_A(n_A, n_B, t) = (1/h_1) V_0 F K_A^+ \cos \theta, \quad (8)$$

$$J_B(n_A, n_B, t) = (1/h_1) V_0 F K_B^+ \sin \theta, \quad (9)$$

where  $V_0 = -\partial\Phi(\xi, t)/\partial\xi$ . The magnitude of the nucleation flux can be expressed as

$$J(n_A, n_B, t) = F_0 K_A^+(n_A^*, n_B^*) \exp(-W^{GK}/kT), \quad (10)$$

where  $K_A^+(n_A^*, n_B^*)$  is the value of  $K_A^+$  at the TSP, whose location is denoted by  $(n_A^*, n_B^*)$ , and  $W^{GK}$  is the generalized kinetic potential. As shown by Li *et al.* [26], the generalized

kinetic potential  $W^{GK}$  consists of a force term  $W_0$ , a kinetic term  $W_1$ , a scaling term  $W_2$ , an anisotropy term  $W_3$ , and the reversible work  $W^{rev}$ :

$$W^{GK} = W^{rev} + W_0 + W_1 + W_2 + W_3, \quad (11)$$

$$W_0 = kT \ln V_0, \quad (12)$$

$$W_1 = -kT \ln K_A^+(n_A, n_B)/K_A^+(n_A^*, n_B^*), \quad (13)$$

$$W_2 = kT \ln h_1, \quad (14)$$

$$W_3 = (kT/2) \ln(\cos^2 \phi + r^{-2} \sin^2 \phi). \quad (15)$$

Note that the kinetic term  $W_1$  defined here is different from that used in other papers [24–26]. This new definition makes the units in Eq. (10) consistent without changing the previous conclusions [24–26]. It should also be noted that Eqs. (8)–(15) are exact results; they are valid for the whole size space and for transient nucleation.

Since nucleation involves barrier crossing kinetics, it should be possible to describe it in terms of an appropriate potential, which we will call the generalized nucleation potential  $W^{GN}$ . The generalized nucleation potential is supposed to satisfy the following requirements: (i) it includes both thermodynamic and kinetic effects; (ii) it reduces to the kinetic potential of the unary system when one of the components vanishes, i.e., when  $r \rightarrow 0$  or  $\infty$ ; and (iii) it has a saddle point through which the major nucleation flux passes. Hereafter, we refer to this saddle point as the genuine saddle point (GSP) as suggested by Nishioka [31].

Obviously, the reversible work  $W^{rev}$  is not this generalized nucleation potential, and neither is the kinetic potential  $W^K = W^{rev} + W_1$ , since it does not always satisfy condition (iii) [25]. The generalized kinetic potential  $W^{GK}$  includes enough information to determine the pathway of the major nucleation flux, but it does not satisfy condition (ii), since the force term  $W_0$  and the scaling term  $W_2$  do not vanish when  $r \rightarrow 0$  or  $\infty$ . This feature becomes more visible if we rewrite the unary nucleation flux as

$$J_u(n_A, t) = F_0 K_u^+(n^*) \exp(-W_u^{GK}/kT), \quad (16)$$

where the subscript ‘‘u’’ denotes the values for the unary system, and  $W_u^{GK}$  is given by

$$W_u^{GK} = W^{rev} + W_1 - kT \ln \frac{\partial}{\partial n_A} \left( \frac{f}{F} \right). \quad (17)$$

Comparing Eqs. (11) and (17), we can see that when  $r \rightarrow 0$ , the  $W_0$  and  $W_2$  terms together reduce to  $-kT \ln(\partial\Phi/\partial n_A)$ , which represents the contribution of the gradient terms. At steady state,  $W_u^{GK} = \text{const}$ , so that there is no extremum on it. When the gradient term is removed,  $W_u^{GK}$  reduces to the kinetic potential  $W^K$ , and the extremum appears. Similarly, in the case of binary nucleation,  $W^{GK}$  is unlikely to possess a saddle point, since the major nucleation flux decreases monotonically along its flow path (see the figures of nucleation flux in Ref. [17]), so condition (iii) is also violated.

Based on the above considerations, we omit the ‘‘gradient terms’’ ( $W_0$  and  $W_2$ ) in Eq. (11) and suggest that the generalized nucleation potential has the form

$$W^{GN} = W^{rev} + W_1 + W_3. \quad (18)$$

The generalized nucleation potential given by Eq. (18) obviously satisfies condition (i). The thermodynamic effect is given by the reversible work  $W^{rev}$  and the kinetic effect by the terms  $W_1$  and  $W_3$ . The attachment kinetics gives rise to  $W_1$ , and  $W_3$  reflects any discrepancy in the impingement rates of the two species. It should also be noted that the anisotropy term  $W_3$  has been shown to be a major cause of ridge crossing [26]. Equation (18) is also consistent with condition (ii). From Eq. (15) we see that when  $\phi=0$ ,  $W_3=0$ . As  $r \rightarrow 0$ , all the nucleation fluxes will lie along the  $n_A$  axis with  $\phi \rightarrow 0$  faster than  $r$ , so that  $W_3=0$ . Our  $W^{GN}$  is also consistent with condition (iii). The pathway of the major nucleation flux corresponds to the valley of the surface of the generalized kinetic potential, and it can be approximately determined by the equation [26]

$$\partial W^{GN} / \partial \eta = 0. \quad (19)$$

As seen from Eq. (12), the force term  $W_0$  is a function that is independent of  $\eta$ , so that  $\partial W_0 / \partial \eta = 0$ . The partial derivative  $\partial W_2 / \partial \eta$  may also be neglected, since Wyslouzil and Wilemski [28,29] numerically found that the  $\Phi$  lines were parallel for the systems that they examined. These numerical results imply that  $h_1$  is approximately constant along each  $\Phi$  line, hence  $\partial W_2 / \partial \eta \approx 0$ . Thus, Eq. (19) may be approximately rewritten as

$$\partial W^{GN} / \partial \eta = 0. \quad (20)$$

Consequently, if  $W^{GN}$  possesses a saddle point, the major nucleation flux determined by Eq. (20) will pass through it. Thus, the generalized nucleation potential  $W^{GN}$  satisfies the conditions (i)–(iii) if the  $\Phi$  lines for a particular binary system are parallel. It should be noted that if the variation of  $W_2$  along a  $\Phi$  line cannot be neglected, it may be necessary to add to  $W^{GN}$  a term corresponding to this variation. In the present paper, we consider only the case that the variation of  $W_2$  along a  $\Phi$  line can be neglected.

If the variation of  $\theta$  is negligibly small in a local region,  $\theta$  can be determined in the whole size space by [32]

$$\tan \theta = [s + (s^2 + r)^{1/2}] / r, \quad (21)$$

where

$$s = -\frac{1}{2} \frac{W_{AA}^K - r W_{BB}^K}{W_{AB}^K}, \quad W_{AA}^K = \frac{\partial^2 W^K}{\partial n_A^2}, \quad (22)$$

$$W_{AB}^K = \frac{\partial^2 W^K}{\partial n_A \partial n_B}, \quad W_{BB}^K = \frac{\partial^2 W^K}{\partial n_B^2}.$$

Thus, the generalized nucleation potential  $W^{GN}$  can be evaluated using Eq. (18) with the help of Eqs. (21) and (22).

Let us consider two examples that demonstrate the value of the genuine saddle point concept. The first one is the ideal ethanol-hexanol system; the other is a model vapor-liquid system (PD2) that exhibits positive deviations from ideality. Both of these systems have been studied in detail by Wyslouzil and Wilemski [17,28,29]. We solve the governing kinetics equations at steady state using the technique of inversion by partition [33] with the reverse rate constants determined by detailed balance and the self-consistent reversible work [29]. Figure 1 shows the locations of the GSP and TSP for a particular set of conditions for each system. For the ideal ethanol-hexanol system, the respective ethanol and hexanol gas phase activities are  $a_E = 1.5$  and  $a_H = 9$  ( $r$  is about 1/56). Figure 1(a) shows the locations of the GSP and TSP for this case as the intersections of the bold contour lines. We also superimpose the contour lines of  $\log_{10} J$  that roughly encompass the region of the major nucleation flux.

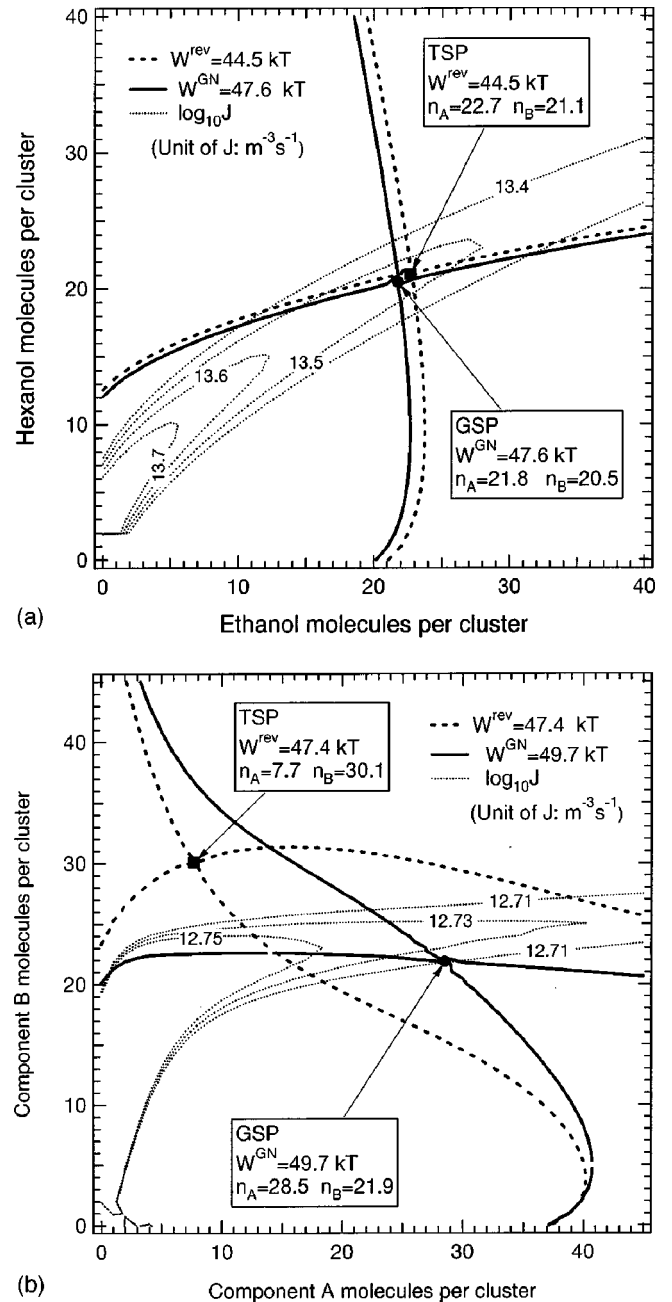


FIG. 1. Locations of the TSP and GSP in the size space. Superimposed are the contour lines of  $\log_{10} J$  that roughly encompass the region of major nucleation flux. (a) Ideal ethanol-hexanol system ( $a_E = 1.5, a_H = 9$ ). (b) PD2 system ( $a_A = 2.25, a_B = 14$ ). The physical properties of these two systems are listed in Ref. [17].

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The location of the GSP ( $n_A=21.8$ ,  $n_B=20.5$ ) is very close to the TSP ( $n_A=22.7$ ,  $n_B=21.1$ ), and the major nucleation flux passes through both of them. Figure 1(b) shows the results for the PD2 system for which the gas phase activities are  $a_A=2.25$  and  $a_B=14$ , respectively, and  $r\approx 1/54$ . We find that the GSP ( $n_A=28.5$ ,  $n_B=21.9$ ) is located far away from the TSP ( $n_A=7.7$ ,  $n_B=30.1$ ). In this case, the major nucleation flux passes through the GSP, evidently bypassing the

TSP [17]. The latter example is particularly important because it illustrates the power of the GSP concept as a simple means of establishing when ridge crossing is occurring.

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