Generalized potentials for a mean-field density functional theory of a three-phase contact line

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We investigate generalized potentials for a mean-field density functional theory of a three-phase contact line. Compared to the symmetrical potential introduced in our previous article [Phys. Rev. E **85**, 011120 (2012)], the three minima of these potentials form a small triangle located arbitrarily within the Gibbs triangle, which is more realistic for ternary fluid systems. We multiply linear functions that vanish at edges and vertices of the small triangle, yielding potentials in the form of quartic polynomials. We find that a subset of such potentials has simple analytic far-field solutions and is a linear transformation of our original potential. By scaling, we can relate their solutions to those of our original potential. For special cases, the lengths of the sides of the small triangle are proportional to the corresponding interfacial tensions. For the case of equal interfacial tensions, we calculate a line tension that is proportional to the area of the small triangle.

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I. INTRODUCTION

In our previous article [1], we treated a three-phase contact line by a mean-field density functional that involves a symmetric potential. This potential allows us to find analytical far-field solutions because one of the mole fractions is constant for any two-phase transition. In order to develop a phenomenological model for a nonsymmetric potential, which is more realistic for ternary fluid systems, we need a more general potential that has three minima in arbitrary locations within the Gibbs triangle. In this article, we introduce a flexible approach to construct such generalized potentials.

As illustrated geometrically in Fig. 1(a), a three-phase contact line is modeled for a ternary fluid system having three bulk phases, α , β , and γ , which subtend dihedral angles θ_{α} , θ_{β} , and θ_{γ} . Each of the interfaces $\alpha\beta$, $\beta\gamma$, and $\gamma\alpha$, if extrapolated far from the contact line, is perpendicular to a side of the dashed triangle, which is illustrative of our much larger actual computational domain. The contact line is where the three interfaces appear to meet. We assume the system to be translationally invariant along the vertical direction perpendicular to this figure, thus reducing this problem to two dimensions. Compared to the homogeneous bulk phases, the inhomogeneity arises from the formation of interfaces and a contact line, which are actually diffuse regions.

Based on the thermodynamic method introduced by Gibbs [2, p. 228], the inhomogeneity is treated by means of an excess grand potential Ω_{xs} , which, by convention [3, chap. 8], can be expressed by

$$\Omega_{\rm xs} = L\tau + LR_{\alpha\beta}\sigma_{\alpha\beta} + LR_{\beta\gamma}\sigma_{\beta\gamma} + LR_{\gamma\alpha}\sigma_{\gamma\alpha}.$$
 (1)

Here *L* is the length of the contact line and R_{ij} is the distance from the contact line along interface ij toward the boundary. In the limit of all $R_{ij} \rightarrow \infty$, the line tension τ is defined as the excess grand potential per unit length associated with the contact line while each of the three interfacial tensions σ_{ij} (excess grand potentials per unit area) is associated with an interface *ij* in the far-field limit. A classical result [4] shows that

$$\frac{\sin \theta_{\alpha}}{\sigma_{\beta\gamma}} = \frac{\sin \theta_{\beta}}{\sigma_{\alpha\gamma}} = \frac{\sin \theta_{\gamma}}{\sigma_{\alpha\beta}}.$$
 (2)

According to this result, the boundary is actually a Neumann triangle since the three sides are proportional to three interfacial tensions.

Besides extensive studies of interfacial tensions (see Ref. [5]), the line tension of a contact line plays a crucial role in a broad range of physical phenomena such as the equilibrium shapes of small droplets [6,7], microfluidics [8,9], heterogeneous nucleation [10], cell adhesion [11], the dynamics of a drop spreading on a liquid thin film [12,13], and the behavior of line tension at wetting transitions [14]. For a review for both experimental and theoretical aspects of line tension, see Ref. [15], and for a conceptual review, see Ref. [16].

A. Mean-field density functional theory

According to the mean-field density functional theory introduced in our earlier work [1], the excess grand potential for a ternary fluid system is

$$\Omega_{\rm xs} = BL \int_A [f+g] \, dA, \tag{3}$$

where *f* is a potential function and *g* is a gradient energy of the chemical constituents. In this article, we assumed that the dominant intermolecular forces in our system are short range, so physical quantities can be formulated in terms of local densities. Based on the assumption of uniform molar volume, we change the variables of *f* and *g* from number densities to mole fractions X_i , and $\sum_{i=1}^3 X_i = 1$ (see Ref. [1, Sec. II] for details). For reviews of the general mean-field density functional method of interfaces, see Refs. [3,17].

In this phenomenological theory, there is no definite form of the potential f for the excess grand potential Ω_{xs} in (3). The specific form that we used in earlier work [1] is

$$f = \sum_{i=1}^{3} (X_i - a)^2 (X_i - b)^2 \equiv f^o,$$
(4)

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FIG. 1. (Color online) Schematic diagram for the mapping between physical space and the Gibbs triangle (briefly, the Gibbs space). (a) Sketch of our system consisting of three bulk phases, α , β , and γ , divided by three interfaces, $\alpha\beta$, $\beta\gamma$, and $\gamma\alpha$. The interfaces, if extrapolated, are each perpendicular to sides of the dashed triangle (illustrative computational domain) and meet at a three-phase contact line. The corresponding dihedral angles are θ_{α} , θ_{β} , and θ_{γ} and (x, y) are Cartesian coordinates in physical space. The region within three solid curves represents approximately the diffuse region of the interfaces and the contact line. (b) The Gibbs space, in which the three bulk phases are located at three points and (u, v)are Cartesian coordinates in units of mole fractions. The three curved lines that connect pairs of points for bulk phases are trajectories of two-phase transitions. (c) Slice of an interface in a cuboid far from the contact line. s is a coordinate perpendicular to the $\alpha\beta$ interface and w is the width of the cuboid in a direction perpendicular to the contact line.

where $0 \le a \le 1$ is a constant and b = (1 - a)/2, is a symmetric quartic function that allowed us to obtain asymptotic analytical solutions in the far field. This form is an extension of the potential used in the Landau's phenomenological theory [18,19]. Similar two-density quartic potentials have been used in Refs. [20,21] for line tension and for a first order wetting transition. Sixth-order polynomials have been used for second-and higher-order transitions [21–23]. In this article, we focus on potentials of quartic form.

Compared to other two-density models, our model is actually pseudobinary since it formulates the potential in terms of three mole fractions $\{X_i\}_{i=1,2,3}$ by the assumption of uniform molar volume. Because of the constraint $\sum_{i=1}^{3} X_i = 1$, there are two independent mole fractions, so our potential can be described in terms of two independent variables, although we sometimes display all three mole factions to illustrate its symmetry.

Note that the gradient energy g in the functional (3) of the excess grand potential Ω_{xs} is specified by

$$g = \sum_{i=1}^{3} \frac{\ell_i^2}{2} |\nabla X_i|^2, \qquad (5)$$

where $\{\ell_i\}_{i=1,2,3}$ are constants. For cases with equal ℓ_i (isotropic gradient energy), the three-fold symmetric potential

leads to threefold symmetry of the physical domain. To resolve this special geometry, we employed a triangular grid to obtain numerical solutions over the entire domain (for details, see Ref. [1, Sec. III]).

B. Mapping from physical space to the Gibbs space

In our mean-field density functional theory of a three-phase contact line for a ternary fluid system (summarized in Sec. I A; for details, see Ref. [1, Sec. II]), the functional of the excess grand potential consists of a potential function and a gradient energy. Since we use three mole fractions as variables, there is a connection between the physical space and the space of the Gibbs triangle (briefly, the Gibbs space). This connection depends on the specific choice of potential and the coefficients of the gradient energy. Figure 1 illustrates a mapping between the physical space of our system [Fig. 1(a)] and the Gibbs space [Fig. 1(b)]. In general, the three bulk phases of the physical system are represented by the three minima of a given potential, which are located at three points within the Gibbs triangle.

The curved lines within the Gibbs triangle [Fig. 1(b)] are the trajectories of the two phase transitions in the far-field regime between any pair of bulk phases in the physical space [Fig. 1(a)]. The far-field regime is located at a distance that is far from the contact line compared to the interfacial widths (or the size of the central core region associated to the contact line). In the far-field regime, a slice of interface can be contained in a cuboid [Fig. 1(c)] and the interfacial width is constant. For a two-phase transition between any pair of bulk phases, the change of mole fractions from one bulk phase to another maps to a curved line connecting two potential minima within the Gibbs triangle. At equilibrium, these trajectories minimize the excess grand potential according to the form of the potential and the coefficients of the gradient energy. Since the interfacial tensions are excess grand potentials per unit area, their values depend on these trajectories.

According to the form (1) of the excess grand potential, the line tension is the residue of excess potential in which we subtract the contribution from the far-field interfacial tensions. In physical space [Fig. 1(a)], it relates to the core of the diffuse region centered at the contact line as if we subtract the cuboids of the interfaces extended from the far-field until they meet at the "contact line." This core region corresponds to threephase transitions among all three bulk phases in the physical space. It can be mapped to a region within the Gibbs triangle [Fig. 1(b)] surrounded by the three trajectories of the two-phase transitions. Similarly to the interfacial tensions, the line tension is the excess grand potential per unit length. Its value depends on the form of the potential within this core area and, of course, the coefficients of gradient energy.

In this article, we extend our previous model to more realistic systems. Specifically, we use geometrical reasoning to construct generalized quartic potentials with three minima arbitrarily located within the Gibbs triangle. For a subset of these potentials, the resulting potential is a linear transformation of our original potential and we can obtain simple analytic far-field solutions. We connect these solutions to our original potential by scaling. For some special cases, we relate interfacial tensions and line tension to the lengths of the sides and the area of the small triangle formed by the three minima.

II. GENERALIZED QUARTIC POTENTIALS

To find more general quartic potentials with arbitrary mimina, while maintaining the condition of constant molar density, we start with a discussion of quartic functions with two independent variables that correspond to two independent mole fractions. In general, a two-variable quartic polynomial can be expressed by

$$f(X,Y) = \sum_{n=0}^{4} \sum_{i=0}^{n} a_{i,n-i} X^{i} Y^{n-i},$$
(6)

which contains 15 independent parameters $a_{i,n-i}$. However, we need a form such that f is positive except for f = 0at the three minima, which gives us three equations relating the coefficients. At each of the minima, we require $\partial f/\partial X =$ $\partial f/\partial Y = 0$, which amounts to six conditions. Furthermore, in order to have parabolic potential wells, we need the second derivatives of f to satisfy the following inequalities at the three minima: $\partial^2 f/\partial X^2 > 0$ (or $\partial^2 f/\partial Y^2 > 0$) and $(\partial^2 f/\partial X^2)(\partial^2 f/\partial Y^2) - (\partial^2 f/\partial X \partial Y)^2 > 0$. This gives us six inequalities. In general, we have 15 - 3 - 6 = 6 free parameters together with six additional constraints.

In this framework, our original potential in (4) is a special case which has only one parameter, *a*, representing the size or orientation (magnification or inversion) of the equilateral triangle formed by the three minima [1, Sec. II A, discussion after Eq. (14)]. In the development to follow, we obtain a positive potential by assuming it to be a sum of squares of various expressions. We break the symmetry of our original potential by locating the three minima at the vertices of a small triangle having any shape and orientation within the Gibbs triangle. In the following discussion, we use the term a "small triangle" to denote an inner triangle formed by the three minima of a given potential within the Gibbs triangle.

A. First generalization

At first, we explore the structure of our original potential f^o in (4). X_i can be expressed as a function of two independent Cartesian variables u and v, i.e., $X_i = X_i(u,v)$ as illustrated in Fig. 1(b). In Ref. [1], we showed that f^o can be scaled to the form

$$\tilde{f} = \frac{f^o}{(a-b)^4} = \sum_{i=1}^3 Y_i(u,v)^2 [Y_i(u,v) - 1]^2,$$
(7)

where $Y_i(u,v) = [X_i(u,v) - b]/(a - b)$ are scaled mole fractions, and $\sum_{i=1}^{3} Y_i = 1$. This form is equivalent to f^o when a = 1. For simplicity, we mainly compare new potentials to \tilde{f} .

As illustrated in Fig. 2(b), we specify explicitly the Cartesian coordinates (u, v) for $Y_i(u, v)$,

$$Y_{1}(u,v) = -\frac{\sqrt{3}}{2}u - \frac{v}{2} + 1,$$

$$Y_{2}(u,v) = \frac{\sqrt{3}}{2}u - \frac{v}{2},$$

$$Y_{3}(u,v) = v.$$
(8)

In (8), the symbols u and v bear the same relationship to the scaled mole fractions Y_i as u and v in Fig. 1(b) do to



(a) Geometry of the three minima of \tilde{f} (or f^o when



FIG. 2. (Color online) (a) Geometry of the three minima of the potential \tilde{f} given by (7) [or f^o in (4) when a = 1]. \tilde{f} is a function of scaled mole fractions $\{Y_i\}_{i=1,2,3}$, where $\sum_{i=1}^{3} Y_i = 1$. Y_i can be expressed in terms of two independent Cartesian coordinates (u, v). $\alpha = (u_1^0, v_1^0) = (0,0), \ \beta = (u_2^0, v_2^0) = (2/\sqrt{3}, 0), \ \text{and} \ \gamma = (u_3^0, v_3^0) = (1/\sqrt{3}, 1)$ are the three minima of \tilde{f} located at the three corners of the Gibbs triangle. $L_i = 0$ represents a line that passes through two points (u_j^0, v_j^0) and (u_k^0, v_k^0) $(j \neq k \neq i)$, and $I_i = 0$ is a line parallel to $L_i = 0$ but passing through only one point (u_i^0, v_i^0) . (b) Contour plot of \tilde{f} . The value of \tilde{f} decreases from its value at the center of the inner area as one proceeds toward the three vertices where it is zero.

the unscaled mole fractions X_i . The three minima of the potential \tilde{f} in (7), namely $\alpha = (u_1^0, v_1^0) = (0,0), \beta = (u_2^0, v_2^0) = (2/\sqrt{3},0)$, and $\gamma = (u_3^0, v_3^0) = (1/\sqrt{3},1)$, are located at the three corners of the Gibbs triangle as in Fig. 2(b), consistent with the contour plot in Fig. 2(a). Note that $Y_i(u_j^0, v_j^0) = Y_i(u_k^0, v_k^0) = 0$ for $j \neq k \neq i$ and $Y_i(u_i^0, v_i^0) = 1$.

If we define two sets of linear functions $L_i^0(u,v) \equiv Y_i(u,v)$ and $I_i^0(u,v) \equiv Y_i(u,v) - 1 = L_i^0(u,v) - 1$, the form (7) of the potential \tilde{f} can be expressed as

$$\tilde{f} = \sum_{i=1}^{3} L_i^0(u, v)^2 I_i^0(u, v)^2.$$
(9)

As shown in Fig. 2(b), $L_i^0 = 0$ is a line in the Gibbs space that passes through two minima (u_j^0, v_j^0) and (u_k^0, v_k^0) , where $j \neq k \neq i$, and $I_i^0 = 0$ is a line parallel to $L_i = 0$ that passes through the remaining minimum (u_i^0, v_i^0) . For each minimum of \tilde{f} , there are three intersecting lines.

Based on the geometrical interpretation of the form (9) of the potential \tilde{f} , we can generalize its structure by allowing these pairs of parallel lines to move and requiring the intersections of three lines to be located within the Gibbs triangle. To generate a potential function with the desired properties, we locate the three minima arbitrarily, $\alpha = (u_1, v_1)$, $\beta = (u_2, v_2)$, and $\gamma = (u_3, v_3)$, within the Gibbs triangle. We then define two sets of linear functions $L_i(u, v)$ and $I_i(u, v)$, where $L_i(u, v) = 0$ is a line passing through two minima (u_j, v_j) and (u_k, v_k) for $j \neq k \neq i$ and $I_i(u, v) = 0$ is a line parallel to $L_i(u, v) = 0$ and passing through the remaining minimum (u_i, v_i) .

As illustrated in Fig. 2(a), the line $L_i = 0$ coincides with the side of the small triangle opposite to the vertex *i*, while the line $I_i = 0$ passes through the vertex *i* and is parallel to the line $L_i = 0$. Thus, a generalized potential with arbitrary mimina is given by

$$f_g = \sum_{i=1}^{3} d_i^2 L_i(u, v)^2 I_i(u, v)^2, \qquad (10)$$

where the d_i are nonzero weighting coefficients that relate to the curvatures along the lines that connect each pair of potential wells. For each term, $L_i(u,v)^2 I_i(u,v)^2$ represents a positive quartic function that vanishes along two parallel lines $L_i(u,v) = 0$ and $I_i(u,v) = 0$. We need all three terms to produce a positive quartic function that vanishes at the three points $(u_i, v_i)_{i=1,2,3}$ which are the intersections of three lines chosen from the three pairs of parallel lines. Contours for such a potential are illustrated in Fig. 3(b).

The choice of $L_i(u,v)$ and $I_i(u,v)$ for the potential f_g in (10) is somewhat arbitrary but we use specific forms of $L_i(u,v)$ and $I_i(u,v)$ and a weighting coefficient for each term to maintain generality. The specific forms of $L_i(u,v)$ and $I_i(u,v)$ that we use are

$$L_{i}(u,v) \equiv C_{ijk}[(u-u_{j})v_{jk} - (v-v_{j})u_{jk}]$$

= $C_{ijk}[(u-u_{k})v_{jk} - (v-v_{k})u_{jk}],$
 $I_{i}(u,v) \equiv L_{i}(u,v) - h$
= $C_{ijk}[(u-u_{i})v_{jk} - (v-v_{i})u_{jk}],$ (11)

where $C_{ijk} \equiv (\epsilon_{ijk} + |\epsilon_{ijk}|)/2$, ϵ_{ijk} is the Levi-Civita symbol for three dimensions, $u_{jk} \equiv u_j - u_k$ and $v_{jk} \equiv v_j - v_k$; moreover, $h = L_i(u_i, v_i) = 2A$, and A is the area of the small triangle. For simplicity, we require the indices of the three vertices to be numbered counterclockwise. Note that

$$h = \sum_{(i,j,k)\in\{1,2,3\}} \epsilon_{ijk} u_j v_k = \begin{vmatrix} 1 & 1 & 1 \\ u_1 & u_2 & u_3 \\ v_1 & v_2 & v_3 \end{vmatrix}.$$
 (12)



FIG. 3. (Color online) (a) Geometry of the three minima of the quartic potential f_g given by (10). $\alpha = (u_1, v_1)$, $\beta = (u_2, v_2)$, and $\gamma = (u_3, v_3)$ are the three minima of this potential arbitrarily located at any three points within the Gibbs triangle. $L_i = 0$ represents a line that passes through (u_j, v_j) and (u_k, v_k) for $j \neq k \neq i$, and $I_i = 0$ is a line parallel to $L_i = 0$ but passing through the vertex (u_i, v_i) . (b) Contour plot of potential f_g for $(u_1, v_1) = (0.3087, 0.1667)$, $(u_2, v_2) = (0.9060, 0.1167)$, $(u_3, v_3) =$ (0.4974, 0.6667), and $(d_1, d_2, d_3) = (1.0, 1.1, 1.2)$.

If we express L_i and h in terms of two independent mole fractions Y_1 and Y_2 , we obtain

$$L_{i} = \frac{2}{\sqrt{3}} C_{ijk} \Big[(Y_{1} - Y_{1}^{(k)}) Y_{2}^{(jk)} - (Y_{2} - Y_{2}^{(k)}) Y_{1}^{(jk)} \Big],$$

$$h = y \frac{2}{\sqrt{3}} \sum_{(i,j,k) \in \{1,2,3\}} \epsilon_{ijk} Y_{1}^{(j)} Y_{2}^{(k)},$$
(13)

in which we have defined $Y_i^{(jk)} \equiv Y_i^{(j)} - Y_i^{(k)}$ and expressed the three minima $(u_i, v_i)_{i=1,2,3}$ in terms of $(Y_1^{(i)}, Y_2^{(i)})_{i=1,2,3}$ by using the relation (8) of (u, v) and Y_i .

The form (10) of the potential f_g has three coefficients d_i and six parameters (u_i, v_i) that locate the positions of the three minima, nine parameters in total. One could take out a common factor without changing the nature of the potential. From the earlier discussion regarding the desired properties of

a general quartic potential given by (6), we know that there are six free parameters, which means there are three parameters that might be able to be merged with others.

From the forms (7) and (9) of the potential \tilde{f} , our original potential f^o divided by a factor $(a - b)^4$ can be viewed as a special case of the potential f_g given by (10), in which the three minima form an equilateral small triangle with one parameter a related to its size. With this parameter, we can scale the small triangle from the Gibbs triangle to its center point with zero area. To add degrees of freedom to allow this equilateral small triangle to move around within the Gibbs triangle, we can add two extra parameters corresponding to translations in two perpendicular directions. For arbitrary shape and orientation of the small triangle, we need a parameter corresponding to rotation and two parameters for distortion, such as changes of two inner angles. In general, these operations correspond to a linear transformation with six free parameters, which will be discussed in Sec. III B.

The general properties of the potential f_g in (10) have been tested by performing calculations of its first and second derivatives with respect to u and v. For details, see Ref. [24, Sec. 5.1.1]. From these calculations, we prove that f_g , which is a generalization of potential \tilde{f} in (7), satisfies our desired properties of a quartic polynomial, as discussed in the beginning of Sec. II. We also calculated the eigenvalues of the Hessian matrix H, which is the matrix in terms of the second derivatives of f_g with respect to u and v. These eigenvalues λ_{\pm} are the principle curvatures at the mimina, i.e.,

$$\begin{aligned} \lambda_{\pm} &= h^2 \left\{ \sum_{i=1}^3 d_i^2 S_i^2 \\ &\pm \sqrt{\left(\sum_{i=1}^3 d_i^2 S_i^2 \right)^2 - 4h^2 \sum_{(i,j,k) \in \{1,2,3\}} C_{i,j,k} d_j^2 d_k^2 } \right\}, \end{aligned}$$
(14)

where $S_i \equiv C_{ijk} \sqrt{u_{jk}^2 + v_{jk}^2}$ is the length of the side of the small triangle opposite to the vertex (u_i, v_i) , as in Fig. 8. Note that both of its eigenvalues λ_{\pm} are positive.

For the case that all $d_i = 1$ and $S_1 = S_2 = S_3 = (2/\sqrt{3})(a-b)$, the eigenvalues of H in (14) reduce to

$$\lambda_{\pm} = \frac{2}{3}(a-b)^6 (2 \pm \sqrt{3}), \tag{15}$$

which connects to our original potential f^o in (4). When a = b = 1/3, these two eigenvalues vanish, which means the curvatures vanish. This is equivalent to the bulk criticality for f^o , for which the three minima merge to a one minimum located at the center of the Gibbs triangle. In this case, the three mole fractions are uniform throughout the physical space, i.e., $X_i = 1/3$. The resulting interfacial and line tensions at the vicinity of this critical value scale consistently with previously determined results in our earlier work [1], in which the ratio of their exponents in terms of $|X_i - 1/3|$ satisfies the mean-field approximation in Ref. [25].

B. Second generalization

The potential f_g in (10) can be generalized by replacing I_i with an arbitrary linear function that passes through a point (u_i, v_i) , which is not necessarily parallel to L_i . For details, see Appendix A. We also observed that $I_i(u,v)^2$ of f_g does not have to vanish on a line $I_i(u,v) = 0$. It can be replaced by a positive quadratic function $K_i(u,v)$ which is a paraboloid in three-dimensional space that vanishes only at the point (u_i, v_i) . In general, $K_i(u,v)$ can be expressed as

$$K_i(u,v) \equiv [a_i(u-u_i) + b_i(v-v_i)]^2 + c_i^2(v-v_i)^2, \quad (16)$$

where a_i , b_i , and c_i are three coefficients and $c_i \neq 0$. Then a more general potential, as illustrated in Fig. 4(a), can be expressed in the form

$$f_G = \sum_{i=1}^{3} L_i(u, v)^2 K_i(u, v).$$
(17)



FIG. 4. (Color online) (a) Geometry of the three minima of the quartic potential f_G given by (17). $\alpha = (u_1, v_1)$, $\beta = (u_2, v_2)$, and $\gamma = (u_3, v_3)$ are the three minima of this potential arbitrarily located at any three points within the Gibbs triangle. $L_i =$ 0 represents a line passing through (u_j, v_j) and (u_k, v_k) , and $K_i = 0$ is a point located at (u_i, v_i) . (b) Contour plot of potential f_G for $(u_1, v_1) = (0.3087, 0.1667)$, $(u_2, v_2) = (0.9060, 0.1167)$, $(u_3, v_3) = (0.4974, 0.6667)$, and $(a_i, b_i, c_i) = (1, 1, 1)$, (i = 1, 2, 3).



FIG. 5. Schematic representation of the generalization from a potential \tilde{f} in (7) to the potential f_g in (10) of similar form and to the more general potential f_G in (17). At the left-hand side of this figure, there are three pairs of two parallel lines. The three minima of \tilde{f} are located at the three nodes where lines intersect and form a small equilateral triangle. In the middle of this figure, we generalize \tilde{f} to f_g by allowing the three minima of f_g to be at arbitrary locations. In this case, the three pairs of parallel lines determine the three minima. The right-hand side of this figure shows a further generalization in which each minimum of f_G is located by two lines and a point.

Of the potentials we have explored f_G in (17) is the most general. It has nine coefficients and six parameters (u_i, v_i) for the positions of the three minima. Thus, it has 15 coefficients in total. We note that when $a_i = C_{ijk}d_iv_{jk}$, $b_i = -C_{ijk}d_iu_{jk}$, and $c_i = 0$, f_G reduces to the potential f_g in (10). Therefore, f_g is a subset of f_G , where f_G has six extra parameters corresponding to the orientations of the three potential wells, as well as the general shape of the potential has to be positive throughout the entire domain and has three minima at zero potential; at these minima, the first derivatives vanish and the Hessien matrices for second derivatives are positive definite. These properties have been tested in Ref. [24, Sec. 5.1.2].

Figure 5 presents a schematic summary of the generalization from the quartic potential \tilde{f} in (7) [equivalent to our original potential f^o in (4) when a = 1] to a similar form (10) of the potential f_g and to a more general quartic form (17) of the potential f_G . In the left-hand side of Fig. 5, we see that the three minima of \tilde{f} form an equilateral small triangle and each minimum is located at an intersection of three lines. These lines consist of three pairs of two parallel lines. For each pair, there is a line passing through two minima and a parallel line passing through the remaining minimum. Each line corresponds to a paraboloid that vanishes at this line, and each pair of parallel lines corresponds to the minima of a quartic function. Thus, \tilde{f} is a sum of three quartic function. As a generalization, in the middle of Fig. 5, the three minima of f_{g} form a small triangle of arbitrary shape. The rules of selecting parallel pairs of lines and constructing corresponding quartic functions for f_g are the same as for \tilde{f} . The right-hand side of Fig. 5 shows a further generalized potential f_G , where each minimum is not located at an intersection of three lines but two lines and a point. In this case, each pair of parallel lines in f_{g} is transformed to a line passing through two minima and a point at the remaining minimum. To compose f_G , we need two sets of quadratic functions. The one in the first set vanishes along a line and the one in the second set vanishes at a point.

III. GENERALIZED POTENTIALS WITH ANALYTIC FAR-FIELD SOLUTIONS

A. Straight-line trajectory of two-phase transition

In Sec. II, we introduced a systematic way to find quartic generalized potentials by means of geometric considerations. In order to find the asymptotic solutions for two-phase transitions in physical space for each of the three interfaces in the regions far from the three-phase contact line, we need to know the corresponding trajectories for transitions between the pairs of wells of a given potential within the Gibbs triangle. According to the discussion in Ref. [24, Sec. 2.4.1], the property of our original potential that leads us to simple far-field analytic solutions is that the trajectory of a transition between any two phases follows a straight line within the Gibbs triangle. From a geometric aspect, this straight line lies along a valley connecting a pair of minima; as one goes along this valley, the potential rises from a minimum, goes over a saddle point, and decreases, to another minimum. The first derivative and the second derivative of the potential with respect to the normal of this straight line in the Gibbs space are zero and positive, respectively. For the subset of generalized potentials that share this common property, we can find analytical far-field solutions. As shown in Appendix B, the form of this subset is actually equivalent to the form (10)of the generalized potential f_g .

B. Linear transformation

According to the geometric representation in Sec. II, as illustrated in Fig. 5, the form (9) of the potential \tilde{f} can be generalized to a similar quartic potential f_g in (10) with arbitrary minima (u_1, v_1) , (u_2, v_2) , and (u_3, v_3) by choosing proper linear functions $L_i(u, v)$ and $I_i(u, v)$. In this way, the obtained potential has six parameters $\{u_i, v_i\}_{i=1,2,3}$ and three weighting coefficients $\{d_i\}_{i=1,2,3}$, which match our earlier reasoning about using six parameters that correspond to operations such as scaling, translation, rotation, and distortion. Furthermore, we notice that these operations may be represented by linear transformations of our original potential.

To construct a linear transformation that maps the three minima from the corners of the Gibbs triangle to three arbitrary internal points (u_1, v_1) , (u_2, v_2) , and (u_3, v_3) as illustrated in



FIG. 6. Schematic linear transformation from the three corners of the Gibbs triangle to three arbitrary internal points (u_1, v_1) , (u_2, v_2) , and (u_3, v_3) within it.

Fig. 6, we write

$$\begin{bmatrix} u'\\v'\end{bmatrix} = \begin{bmatrix} \alpha & \beta\\\gamma & \delta\end{bmatrix} \begin{bmatrix} u\\v\end{bmatrix} + \begin{bmatrix} \xi\\\eta\end{bmatrix}, \quad (18)$$

where α , β , γ , δ , ξ , and η are six undetermined parameters. By substituting (u_1, v_1) , (u_2, v_2) , and (u_3, v_3) for (u', v'), and the corresponding three corners (0,0), $(2/\sqrt{3},0)$, and $(1/\sqrt{3},1)$ for (u,v), we solve

$$\begin{bmatrix} u'\\v'\end{bmatrix} = \begin{bmatrix} -\frac{\sqrt{3}}{2}u_{12} & \frac{1}{2}u_{12} + u_{31}\\ -\frac{\sqrt{3}}{2}v_{12} & \frac{1}{2}v_{12} + v_{31} \end{bmatrix} \begin{bmatrix} u\\v\end{bmatrix} + \begin{bmatrix} u_1\\v_1\end{bmatrix}, \quad (19)$$

where $u_{ij} \equiv u_i - u_j$ and $v_{ij} \equiv v_i - v_j$. Then, by matrix inversion, we find

$$\begin{bmatrix} u \\ v \end{bmatrix} = \frac{2}{\sqrt{3}h} \begin{bmatrix} \frac{1}{2}v_{12} + v_{31} & -\frac{1}{2}u_{12} - u_{31} \\ \frac{\sqrt{3}}{2}v_{12} & -\frac{\sqrt{3}}{2}u_{12} \end{bmatrix} \begin{bmatrix} u' - u_1 \\ v' - v_1 \end{bmatrix}, \quad (20)$$

where $h \neq 0$ is twice the area of the small triangle, defined in (11) and (12).

A generalization of the potential \tilde{f} in (7) with weighting coefficients e_i can be expressed in terms of two independent Cartesian mole fractions u and v as follows:

$$f^{\dagger}(u,v) \equiv f^{\dagger}(Y_{1}(u,v), Y_{2}(u,v), Y_{3}(u,v))$$
$$\equiv \sum_{i=1}^{3} e_{i}^{2} Y_{i}(u,v)^{2} (Y_{i}(u,v)-1)^{2}.$$
(21)

To construct a new potential with three minima located at $(u_1, v_1), (u_2, v_2)$, and (u_3, v_3) , we replace $Y_i(u, v)$ in (21) by

$$Z_i(u',v') \equiv Y_i(u(u',v'),v(u',v')),$$
(22)

where the linear transformation (20) from (u',v') to (u,v) has been used. We then (see Ref. [24] for details) find (after dropping the primes)

$$Z_i(u,v) = \frac{L_i(u,v)}{h},$$
(23)

where, as defined in (11), L_i is a linear function that satisfies $L_i(u_j, v_j) = 0$ and $L_i(u_k, v_k) = 0$ for $(j \neq k \neq i)$, whereas $L_i(u_i, v_i) = h$, which leads to $Z_i(u_i, v_i) = 1$. Note that $\sum_{i=1}^{3} Z_i = 1$. Thus, the new potential is defined as

$$f^{*}(u,v) \equiv f^{\dagger}(Z_{1}(u,v), Z_{2}(u,v), Z_{3}(u,v))$$

= $\sum_{i=1}^{3} e_{i}^{2} Z_{i}(u,v)^{2} [Z_{i}(u,v) - 1].$ (24)

With the definition (24) of the new potential f^* , we find that $\{f^*(u_i, v_i) = 0\}_{i=1,2,3}$, which shows that the three mimina of f^* are located at $\{(u_i, v_i)\}_{i=1,2,3}$. By expressing f^* , which relates to the potential f^{\dagger} in (21) [generalized from the potential \tilde{f} in (7)] by a linear transformation, in terms of L_i , i.e.,

$$f^* = \sum_{i=1}^{3} \frac{e_i^2}{h^4} L_i^2 (L_i - h)^2 = \sum_{i=1}^{3} d_i^2 L_i^2 I_i^2 = f_g, \quad (25)$$

where $d_i \equiv e_i/h^2$, we obtain exactly the potential f_g in (9). Thus, f_g is a linear transformation from the original potential \tilde{f} with extra weighting coefficients. This is the reason that \tilde{f} and f_g share a common property: the two-phase transitions in the physical domain follow straight lines in the Gibbs space.

Notice that the structure of the two-density quartic potential used by Widom *et al.* [20,21] actually belongs to the general category indicated by the form (10) of the potential f_g . The two relative densities of their potential can be treated as our two Cartesian mole fractions u and v. We can scale their potential in terms of three dimensionless quantities similar to the Z_i in our expression and obtain a form similar to f_g . However, their systems do not follow the assumption of uniform molar volume. Therefore, in their systems, the sum of the quantities $\sum_{i=1}^{3} Z_i \neq 1$ and cannot be mapped into our potentials.

C. Scaling

From Sec. III B, we know that the potential f_g in (10) and the potential \tilde{f} in (7) can be connected by a linear transformation. In general, a problem involved f_g can be solved by scaling into a form like \tilde{f} , which we studied in Ref. [1, Sec. IVC]. As an example, we consider the excess grand potential given by (3) but with $f \rightarrow f_g$, namely

$$\hat{\Omega}_{\rm xs} = BL \int_A [f_g(u,v) + g(\nabla u, \nabla v)] dA.$$
⁽²⁶⁾

We express the gradient energy in terms of two Cartesian mole fractions u and v,

$$g(\nabla u, \nabla v) = \epsilon_u |\nabla u|^2 + \epsilon_v |\nabla v|^2 + \epsilon_{uv} (\nabla u \cdot \nabla v), \quad (27)$$

where $\epsilon_u = (3/8)(\ell_1^2 + \ell_2^2)$, $\epsilon_v = (1/8)(\ell_1^2 + \ell_2^2) + (1/2)\ell_3^2$, and $\epsilon_{uv} = (\sqrt{3}/4)(\ell_1^2 - \ell_2^2)$. For isotropic gradient energy, $\ell_i \equiv \ell$, we have $\epsilon_u = \epsilon_v = (3/4)\ell^2$ and $\epsilon_{uv} = 0$. According to the scaling (23) from (u, v) to L_i , we can express $\hat{\Omega}_{xs}$ as

$$\hat{\Omega}_{xs} = BL \int_{A} \left[\sum_{i=1}^{3} d_{i}^{2} L_{i}^{2} I_{i}^{2} + g(\nabla u, \nabla v) \right] dA$$

$$= BLh^{4} \int_{A} \sum_{i=1}^{3} \left[d_{i}^{2} Z_{i}^{2} (Z_{i} - 1)^{2} + \frac{\hat{\ell}_{i}^{2}}{2} |\nabla Z_{i}|^{2} \right] dA,$$
(28)

where

$$\hat{\ell}_{1}^{2} = -\frac{2}{h^{4}} \bigg[\epsilon_{u} u_{12} u_{31} + \epsilon_{v} v_{12} v_{31} + \frac{\epsilon_{uv}}{2} (u_{12} v_{31} + v_{12} u_{31}) \bigg],$$

$$\hat{\ell}_{2}^{2} = -\frac{2}{h^{4}} \bigg[\epsilon_{u} u_{23} u_{12} + \epsilon_{v} v_{23} v_{12} + \frac{\epsilon_{uv}}{2} (u_{23} v_{12} + v_{23} u_{12}) \bigg],$$

$$\hat{\ell}_{3}^{2} = -\frac{2}{h^{4}} \bigg[\epsilon_{u} u_{31} u_{23} + \epsilon_{v} v_{31} v_{23} + \frac{\epsilon_{uv}}{2} (u_{31} v_{23} + v_{31} u_{23}) \bigg].$$

$$(29)$$

1. Case $d_i = 1$

Consider a special case of the potential f_g in (10) when all of the weighting coefficients are equal to 1, i.e., $d_i = 1$. According to the asymptotic analysis in our previous work [1, Sec. IIC], we know how to obtain analytical solutions for twophase transitions in a region far from the three-phase contact line for the form (28) of the excess grand potential $\hat{\Omega}_{xs}$. These solutions show that the interfacial tension $\hat{\sigma}_{\alpha\beta}$ is proportional to $\sqrt{\hat{\ell}_1^2 + \hat{\ell}_2^2}$ and the similar relations applied to $\hat{\sigma}_{\gamma\alpha}$ and $\hat{\sigma}_{\beta\gamma}$ {see Ref. [1, Eq. (25)]}. Therefore, we can express the relation (2) of the dihedral angles and the interfacial tensions as follows:

$$\frac{\sin \theta_{\alpha}}{\sqrt{\hat{\ell}_{2}^{2} + \hat{\ell}_{3}^{2}}} = \frac{\sin \theta_{\beta}}{\sqrt{\hat{\ell}_{3}^{2} + \hat{\ell}_{1}^{2}}} = \frac{\sin \theta_{\gamma}}{\sqrt{\hat{\ell}_{1}^{2} + \hat{\ell}_{2}^{2}}},$$
(30)

in which the denominators can be obtained by calculating the sums of pairs of $\hat{\ell}_i^2$ in (29),

$$\hat{\ell}_{1}^{2} + \hat{\ell}_{2}^{2} = \frac{2}{h^{4}} [\epsilon_{u} u_{12}^{2} + \epsilon_{v} v_{12}^{2} + \epsilon_{uv} u_{12} v_{12}],$$

$$\hat{\ell}_{2}^{2} + \hat{\ell}_{3}^{2} = \frac{2}{h^{4}} [\epsilon_{u} u_{23}^{2} + \epsilon_{v} v_{23}^{2} + \epsilon_{uv} u_{23} v_{23}], \qquad (31)$$

$$\hat{\ell}_{3}^{2} + \hat{\ell}_{1}^{2} = \frac{2}{h^{4}} [\epsilon_{u} u_{31}^{2} + \epsilon_{v} v_{31}^{2} + \epsilon_{uv} u_{31} v_{31}].$$

2. Case $d_i = 1$ and $\ell_i = \ell$

Following the discussion in Sec. III C2 for the special case with equal weighting coefficients $d_i = 1$ of the potential f_g in (10), a subset of this special case possesses an interesting property. This subset is specified by assuming the gradient energy g in (27) is isotropic, given by $\ell_i = \ell$. The sums of pairs of ℓ_i^2 in (31) then become

$$\hat{\ell}_{1}^{2} + \hat{\ell}_{2}^{2} = \frac{3\ell^{2}}{2h^{4}} [u_{12}^{2} + v_{12}^{2}] = \frac{3\ell^{2}}{2h^{4}} S_{3}^{2},$$

$$\hat{\ell}_{2}^{2} + \hat{\ell}_{3}^{2} = \frac{3\ell^{2}}{2h^{4}} [u_{23}^{2} + v_{23}^{2}] = \frac{3\ell^{2}}{2h^{4}} S_{1}^{2},$$

$$\hat{\ell}_{3}^{2} + \hat{\ell}_{1}^{2} = \frac{3\ell^{2}}{2h^{4}} [u_{31}^{2} + v_{31}^{2}] = \frac{3\ell^{2}}{2h^{4}} S_{2}^{2},$$

$$(32)$$

where S_i is the length of the side of the small triangle opposite to the vertex (u_i, v_i) , defined earlier in the expression (14) for the eigenvalues λ_{\pm} of the Hessian matrix of f_g . The relation of dihedral angles in (30) then reduces to

$$\frac{\sin\theta_{\alpha}}{S_1} = \frac{\sin\theta_{\beta}}{S_2} = \frac{\sin\theta_{\gamma}}{S_3}.$$
(33)

Therefore, for this special case, the sine of each dihedral angle of a bulk phase is proportional to the length of the side of the small triangle opposite to the vertex corresponding to the given bulk phase. This is illustrated in Fig. 8 and will be revisited in Sec. IV A.

Notice that, in general, $\hat{\ell}_1 \neq \hat{\ell}_2 \neq \hat{\ell}_3$ in (32), which leads to the lengths S_i of the three edges of the small triangle unequal. According to the relation (33) of the dihedral angles and S_i , the three dihedral angles differ. Therefore, f_g is capable of representing an asymmetric three-phase contact line with isotropic gradient energy.

D. Asymptotic far-field solutions

Alternatively, we can find the relationship of the dihedral angles of a system specified by the potential f_g in (10) directly. We consider a transition from phase $\beta = (u_2, v_2)$ to phase $\alpha = (u_1, v_1)$, which follows a straight line $L_3 = 0$ within the Gibbs triangle as illustrated in Fig. 3(a). In the far-field limit, the transition occurs in a regime far from the three-phase contact line in the physical space. In this regime, the three mole fractions Y_i satisfy the boundary condition $\nabla Y_i \cdot \hat{n} = 0$. By assuming $u_{12} \neq 0$, we can interchange v with u according to $L_3 = 0$, i.e., $v - v_2 = (v_{12}/u_{12})(u - u_2)$ and $v - v_1 = (v_{12}/u_{12})(u - u_1)$. The problem then is essentially a one-dimensional problem. The excess grand potential $\hat{\Omega}_{xs}$ in (28) reduces to the form

$$\hat{\Omega}_{\rm xs} = BLw \left(\frac{h}{u_{12}}\right)^4 \int \left[H(u) + \hat{\epsilon}_{uv} \left(\frac{du}{ds}\right)^2\right] ds, \quad (34)$$

where *s* is a coordinate perpendicular to the $\alpha\beta$ interface measured from β to α and *w* is the width of an area in the far-field regime as illustrated in the bottom of Fig. 1 (for details, see Ref. [1, Fig. 4]), $H(u) \equiv (d_1^2 + d_2^2)(u - u_1)^2(u - u_2)^2$, and $\hat{\epsilon}_{uv} = (u_{12}^2/h^4)(\epsilon_u u_{12}^2 + \epsilon_v v_{12}^2 + \epsilon_{uv} u_{12} v_{12})$. The limits of integration are effectively from $-\infty$ to ∞ .

Following the variational method introduced in Ref. [1, Sec. II.C] (details in Ref. [24, Sec. 5.2.3]), we obtain the far-field solution for u at the $\alpha\beta$ interface,

$$u(s) = \frac{u_1 + u_2}{2} + \frac{u_1 - u_2}{2} \tanh\left[\frac{s}{\delta_{\text{int},\alpha\beta}}\right],$$
 (35)

where we choose s = 0 as $u = (u_1 + u_2)/2$ and define the interfacial width parameter of the $\alpha\beta$ interface as

$$\delta_{\text{int},\alpha\beta} \equiv \frac{2}{|u_{12}|} \sqrt{\frac{\hat{\epsilon}_{uv}}{\left(d_1^2 + d_2^2\right)}} = \sqrt{2} \sqrt{\frac{\hat{\ell}_1^2 + \hat{\ell}_2^2}{d_1^2 + d_2^2}}.$$
 (36)

Alternatively, if $u_{12} = 0$, we can use the relation of $L_3 = 0$ to obtain v(s) for the $\alpha\beta$ interface

$$v(s) = \frac{v_1 + v_2}{2} + \frac{v_1 - v_2}{2} \tanh\left[\frac{s}{\delta_{\text{int},\alpha\beta}}\right].$$
 (37)

Figure 7 illustrates the analytic far-field solutions for the mole fraction Y_i at the $\alpha\beta$ interface for the special case in which all of the weighting coefficient are constants, $d_i = 1$, and the gradient energy is isotropic, $\ell_i = 1$ ($\epsilon_u = \epsilon_v = 3/4$ and $\epsilon_{uv} =$



FIG. 7. Analytic far-field solutions for the mole fraction Y_i for a special case of the potential f_g in (10) at the $\alpha\beta$ interface. In this special case, $d_i = 1$ and $\ell_i = 1$ ($\epsilon_u = \epsilon_v = 3/4$ and $\epsilon_{uv} = 0$). The three minima of f_g are $(u_1, v_1) = (0.3087, 0.1667)$, $(u_2, v_2) =$ (0.9060, 0.1167), and $(u_3, v_3) = (0.4974, 0.6667)$.

0). Compared to the similar analytic far-field solutions for our original potential f^o given by (4) in Ref. [1, Fig. 5], the mole fraction Y_3 is no longer a constant and, in general, the solutions for Y_1 and Y_2 are not symmetric with respect to the interface.

The interfacial tension of the $\alpha\beta$ interface in the far-field limit is given by

$$\hat{\sigma}_{\alpha\beta} = \frac{\sqrt{(d_1^2 + d_2^2)\hat{\epsilon}_{uv}}}{3|u_{12}|} Bh^4 = \frac{\sqrt{(d_1^2 + d_2^2)(\hat{\ell}_1^2 + \hat{\ell}_2^2)}}{3\sqrt{2}} Bh^4.$$
(38)

We can calculate the interfacial tensions of the $\beta\gamma$ interface and the $\gamma\alpha$ interface by the same method. Compared to the previous result (30) of the equilibrium dihedral angles for a system with potential f_g , a more general relation obeys

$$\frac{\sin \theta_{\alpha}}{\sqrt{(d_2^2 + d_3^2)(\hat{\ell}_2^2 + \hat{\ell}_3^2)}} = \frac{\sin \theta_{\beta}}{\sqrt{(d_3^2 + d_1^2)(\hat{\ell}_3^2 + \hat{\ell}_1^2)}}$$
$$= \frac{\sin \theta_{\gamma}}{\sqrt{(d_1^2 + d_2^2)(\hat{\ell}_1^2 + \hat{\ell}_2^2)}}.$$
 (39)

IV. GEOMETRY OF INTERFACIAL TENSION AND LINE TENSION

Recall the discussion of the mapping from the physical space to the Gibbs space in Sec. I B. In a ternary fluid system with three phases, the interfacial tensions associated with the three interfaces correspond to curved lines (trajectories) within the Gibbs triangle that connect the three minima of a given potential. Each trajectory can be obtained by minimizing the excess grand potential for a two-phase transition in a far-field limit. These trajectories bound a region of the Gibbs space that associates with three-phase transitions. Consequently, the line tension associated with the three-phase contact line is determined by the excess grand potential within this region. This mapping implies a geometrical relationship among the values of interfacial and line tensions and the size and shape of the core area.

Here we demonstrate this geometrical connection by some special cases of the specific potential f_g given by (10), in which the core area is the small triangle formed by the minima of the potential within the Gibbs triangle.

A. Case $d_i = 1$ and $\ell_i = \ell$

As shown in Sec. III A, for the potential f_g in (10), the trajectory for a two-phase transition follows a straight line. In the special case of f_g discussed in Sec. III C2, all of the weighting coefficients $d_i = 1$ and the gradient energy is isotropic, $\ell_i = \ell$. Compared to the form (2) of the classical result, in which the sine of a dihedral angle is proportional to a corresponding interfacial tension, the relation in (33) indicates that the sine of a dihedral angle is proportional to the length of the side of the small triangle, within the Gibbs triangle, opposite to the vertex for the corresponding bulk phase. This leads to the fact that the three interfacial tensions are proportional to the three lengths of the sides of the small triangle is a Neumann triangle, which is similar to the computational boundary of the physical domain [see Figs. 1(a) and 8].



FIG. 8. Geometry of the three interfacial tensions in the Gibbs space for a special case of the potential f_g given by (10), in which the weighting coefficients are equal to 1, $d_i = 1$, and the gradient energy is isotropic, $\ell_i = 1$. The three vertices 1, 2, and 3 correspond to the three minima α , β , and γ of f_g . The length of the side of the small triangle opposite to the vertex *i* is labeled by S_i , and the area of the small triangle is *A*. The interfacial tension of the $\alpha\beta$ interface $\hat{\sigma}_{\alpha\beta}$ is proportional to the length of the side of the small triangle that connects α and β , i.e., S_3 . Similarly, $\hat{\sigma}_{\beta\gamma} \propto S_1$ and $\hat{\sigma}_{\gamma\alpha} \propto S_2$. θ_{α} , θ_{β} , and θ_{γ} are the three dihedral angles corresponding to the three-phase contact line.

To prove this property explicitly, we substitute $\hat{\ell}_1^2 + \hat{\ell}_2^2$ from (38) into (32) to obtain

$$\hat{\sigma}_{\alpha\beta} = \frac{B\ell}{\sqrt{6}} h^2 S_3. \tag{40}$$

Similarly, for the $\beta\gamma$ interface and $\gamma\alpha$ interfaces, the tensions are

$$\hat{\sigma}_{\beta\gamma} = \frac{B\ell}{\sqrt{6}} h^2 S_1$$
 and $\hat{\sigma}_{\gamma\alpha} = \frac{B\ell}{\sqrt{6}} h^2 S_2.$ (41)

B. Case $d_i = 1$, $\ell_i = \ell$, and $S_i = S$

We consider a subset of the case treated in Sec. IV A, in which the small triangle formed by the three minima of the potential f_g in (10) is equilateral, i.e., $S_i \equiv S$. The area of the small triangle then is

$$A = \frac{h}{2} = \frac{\sqrt{3}}{4}S^2.$$
 (42)

From the relation (32) between the sums of pairs of $\hat{\ell}_i^2$ and S_i , we find that

$$\hat{\ell}_i^2 \equiv \hat{\ell}^2 = \frac{3\ell^2}{2h^4} \frac{S^2}{2} = \frac{3\ell^2}{2h^4} \frac{h}{\sqrt{3}} = \frac{\sqrt{3}\ell^2}{2h^3}.$$
 (43)

According to the form (26) of the excess grand potential $\hat{\Omega}_{xs}$, we use the Kerins-Boiteux formula [26] to obtain a line



FIG. 9. Geometry of the line tension in the Gibbs triangle for a special case of f_g with equal weighting coefficients $d_i = 1$, isotropic gradient energy $\ell_i = \ell$, and the small triangle formed by the three minima is equilateral. The line tension and the interfacial tensions are proportional to the area *A* and the lengths of the sides of the small triangle, respectively.

tension associated with the three-phase contact line,

$$\begin{aligned} \hat{\tau} &= B \int_{A} [-f_{g}(u,v) + g(\nabla u, \nabla v)] dA, \\ &= B h^{4} \int_{A} \sum_{i=1}^{3} \left[-Z_{i}^{2} (Z_{i}-1)^{2} + \frac{\hat{\ell}^{2}}{2} |\nabla Z_{i}|^{2} \right] dA, \\ &= B h^{4} \hat{\ell}^{2} \tilde{\tau}, \end{aligned}$$
(44)

where $\tilde{\tau}$ is the dimensionless quantity introduced in Ref. [1, Eq. (53)]. From the expressions for area *A* in (42) and $\hat{\ell}^2$ in (43), we then find

$$\hat{\tau} = \sqrt{3}AB\ell^2\tilde{\tau},\tag{45}$$

which is proportional to the area of the small triangle, as illustrated in Fig. 9.

From above cases, the small triangle in the Gibbs space not only tells us the compositions of the three bulk phases in terms of mole fractions from the locations of its three vertices, but also its size and shape give us information about the equilibrium dihedral angles and the relative strengths of the interfacial tensions. Moreover, the line tension is proportional to the area of this small triangle.

V. SUMMARY AND CONCLUSIONS

We are interested in potentials that are positive semidefinite that vanish only at three mimima. Moreover, we choose to deal with potentials that vary quadratically around the three minima. We seek potentials in the form of quartic polynomials. Our original potential [1] is the sum of three quartic polynomials, each of which vanishes along two parallel lines in the Gibbs triangle. The three minima of our potential are located at the intersections of any three among these six lines. By recognizing this geometrical structure, we can PHYSICAL REVIEW E 88, 012117 (2013)

construct generalized quartic potentials with three minima arbitrarily located at the vertices of a small triangle within the Gibbs triangle.

As a first generalization, for each vertex, we can choose a linear function that vanishes along a line that passes through a pair of vertices and another linear function that vanishes along a parallel line that passes through the remaining vertex. The squares of these two linear functions form paraboloids that vanish at these two lines. We use the product of these two paraboloids to construct one of the three quartic polynomials whose sum is the generalized potential. By performing similar constructions at the other two vertex pairs, we can build a potential which is the sum of three quartic polynomials that vanishes at only three points. Our original potential belongs to a subset of this generalization where the two "vanishing lines" of each quartic polynomials are parallel. To construct a potential in this subset, we need six parameters, namely the coordinates of the three minima and three weighting coefficients for each quartic polynomials. However, we find that each paraboloid that vanishes at a line passing through one vertex can be generalized to another paraboloid that only vanishes at a point, the vertex. By means of this second generalization, we construct another potential with nine parameters related to the shapes of the new paraboloids and containing six parameters to characterize the three minima. We check the properties of these generalized potentials by studying their first and second derivatives.

Generalized potentials in which the valleys connecting any of the two minima follow straight lines in the Gibbs triangle have simple analytic far-field solutions. We prove that this subset of generalized potentials is a special case of our first generalization that was constructed by three pairs of parallel lines. Analytic far-field solutions of this subset are presented. Moreover, we find that this subset is a linear transformation of our original potential. By scaling, we can relate their solutions to those for our original potential. When the weighting coefficients of the potentials in this subset are equal and the gradient energy is isotropic, the lengths of the sides of the small triangle formed by the three minima are proportional to the corresponding interfacial tensions. For the case of equal interfacial tensions, we are able to calculate a line tension that is proportional to the area of the small triangle.

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APPENDIX A

We can generalize the potential f_g in (10) by replacing I_i with an arbitrary linear function J_i that passes through (u_i, v_i) . If $J_i(u, v) \equiv a_i(u - u_i) + b_i(v - v_i)$, where a_i and b_i are arbitrary constants, we can obtain a generalized



FIG. 10. (Color online) (a) Geometry of the three minima of the quartic potential f_1 given by (A1). $\alpha = (u_1, v_1)$, $\beta = (u_2, v_2)$, and $\gamma = (u_3, v_3)$ are the three minima of this potential arbitrarily located at any three points in Gibbs space. $L_i = 0$ represents a line that passes through (u_j, v_j) and (u_k, v_k) for $j \neq k \neq i$. (b) Contour plot of potential f_1 for $(u_1, v_1) = (0.3087, 0.1667), (u_1, v_1) = (0.3087, 0.1667), (u_2, v_2) = (0.9060, 0.1167), (u_3, v_3) = (0.4974, 0.6667), and <math>(a_1, b_1) = (1, 0.1), (a_2, b_2) = (-1, 0.1), and <math>(a_3, b_3) = (-0.1, 1).$

potential,

$$f_1 = \sum_{i=1}^{3} L_i(u, v)^2 J_i(u, v)^2,$$
(A1)

as illustrated in Fig. 10(a). In this case, $J_i = 0$ and $L_i = 0$ do not need to be parallel.

For the special case in which J_1 , J_2 , and J_3 match with L_2 , L_3 , and L_1 , we can define a potential that employs only three lines, namely

$$f_{2} = d_{12}^{2} L_{1}(u, v)^{2} L_{2}(u, v)^{2} + d_{23}^{2} L_{2}(u, v)^{2} L_{3}(u, v)^{2} + d_{31}^{2} L_{3}(u, v)^{2} L_{1}(u, v)^{2},$$
(A2)

where d_{12} , d_{23} , and d_{31} are weighting coefficients. At each minimum, only two lines meet as illustrated in Fig. 11(a). The contours of potential f_2 are shown in Fig. 11(b).



FIG. 11. (Color online) (a) Geometry of the three minima of the quartic potential f_2 given by (A2). $\alpha = (u_1, v_1)$, $\beta = (u_2, v_2)$, and $\gamma = (u_3, v_3)$ are the three minima of this potential arbitrarily located at any three points in Gibbs space. $L_i = 0$ represents a line that passes through (u_j, v_j) and (u_k, v_k) for $j \neq k \neq i$. (b) Contour plot of potential f_2 for $(u_1, v_1) = (0.3087, 0.1667)$, $(u_1, v_1) = (0.3087, 0.1667)$, $(u_2, v_2) = (0.9060, 0.1167)$, $(u_3, v_3) =$ (0.4974, 0.6667), and $d_{12} = d_{23} = d_{31} = 1$.

Note that f_1 in (A1) and f_2 in (A2) are special cases of the potential f_G defined in (17).

APPENDIX B

To study the general form of the subset of generalized potentials in which any two-phase transition follows a straight line, we explore the transition between two phases by means of a potential f_{2D} that is a quartic function of three mole fractions having three minima (u_1, v_1) , (u_2, v_2) , and (u_3, v_3) located at the three vertices of the Gibbs triangle. The potential function along any two of the three wells actually reduces to a one-dimensional potential f_{1D} . Consider the transition from (u_1, v_1) to (u_2, v_2) that follows a straight line $L_3 = 0$. We

let

$$f_{2D}|_{L_3=0}(u,v) = f_{1D},\tag{B1}$$

where f_{1D} is a positive quartic potential function having two minima at (u_1, v_1) and (u_2, v_2) . Since f_{1D} follows a straight line $L_3 = 0$ within the Gibbs triangle, we can express f_{1D} as a function of one variable. We then let

$$f_{1D}(u) = (u - u_1)(u - u_2)g(u),$$
 (B2)

where g(u) is a quadratic function of u. By requiring $\partial f_{1D}/\partial u = 0$ at u_1 and u_2 and $\partial^2 f_{1D}/\partial u^2 > 0$, we obtain

$$f_{1D}(u) \propto (u - u_1)^2 (u - u_2)^2.$$
 (B3)

We can generalize the contribution of $f_{1D}(u)$ to $f_{2D}(u,v)$, which is denoted as $f_{2D}^{(1)}$ by combination of $L_1(u,v)$ and $K_1(u,v)$, i.e.,

$$f_{2D}^{(1)} = L_1^2(u, v) K_1(u, v), \tag{B4}$$

similarly to the potential f_G in (17), which vanishes at the three minima. However, if the transition between (u_1, v_1) and (u_2, v_2) follows the straight line $L_3 = 0$, we need

$$\frac{\partial L_1^2(u,v)K_1(u,v)}{\partial \hat{L}_3}\Big|_{L_3=0},$$
(B5)

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where $\hat{L}_3 \equiv (v_{12}, -u_{12})$ is a normal vector perpendicular to $L_3 = 0$ in the Gibbs space. Thus, we calculate

$$\frac{\partial (L_1^2 K_1)}{\partial \hat{L}_3} \Big|_{L_3=0}$$

$$= 2 \left(\frac{h}{v_{12}} \right) (v - v_1)(v - v_2)$$

$$\times \left\{ (v_{12})^2 \left[\left(a_1 \frac{u_{12}}{v_{12}} + b_1 \right)^2 + c_1^2 \right] (v - v_1) - u_{12} \left(\frac{h}{v_{12}} \right) \left[a_1 b_1 \frac{u_{12}}{v_{12}} + b_1^2 + c_1^2 \right] (v - v_2) \right\}, \quad (B6)$$

in which we substitute $(u - u_1) = (u_{12}/v_{12})(v - v_1)$ for $L_3 = 0$ by assuming $v_{12} \neq 0$. In general, $h \neq 0$, $u_{12} \neq 0$, $(v - v_1) \neq 0$, and $(v - v_2) \neq 0$. The nontrivial solution for (B5) is $a_1 = v_{12}$, $b_1 = -u_{12}$, and $c_1 = 0$. Then, $f_{2D}^{(1)}$ reduces to

$$f_{2D}^{(1)} = L_1(u, v)^2 I_1(u, v)^2.$$
(B7)

Similarly, we can apply this same analysis to the transitions of $(u_2, v_2) \leftrightarrow (u_3, v_3)$ and $(u_3, v_3) \leftrightarrow (u_1, v_1)$. Thus, we conclude that

$$f_{2D} = f_g. \tag{B8}$$

In Sec. II, we have shown that the potential f_g has our desired properties. Moreover, the two-phase transitions of f_g follow straight lines in the space of the Gibbs triangle, which allows us to find analytical solutions in the far field.

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