Letters

A thermodynamic derivation of the dihedral angle equation for a two phase system

It is well-known that in a two phase (solid–liquid or solid–vapour) two particle system, a dihedral angle, ϕ, forms as seen for an ideal system in Fig. 1. If it is *assumed* for the purposes of derivation that the particles, S, are of uniform spherical size, free of gravitational effects and are crystalline with isotropic interfacial energies, the system will be completely symmetrical with a unique dihedral angle, ϕ, determined by the following expression

$$\gamma_{SS} = 2\gamma_{SF} \cos\frac{\phi}{2} \qquad (1)$$

where γ_{SS} is the specific interfacial energy* at the solid–solid interface, i.e. the grain boundary energy, and γ_{SF} is the specific interfacial energy at solid–fluid (vapour or liquid) interface. (In real systems dihedral angles would be achieved but symmetrical configurations would almost never be reached because of the anisotropy of the surface and grain boundary energies, both of which are dependent on crystallographic orientations, and because of intermediate metastable configurations due to kinetics affected by differences in mass transport.)

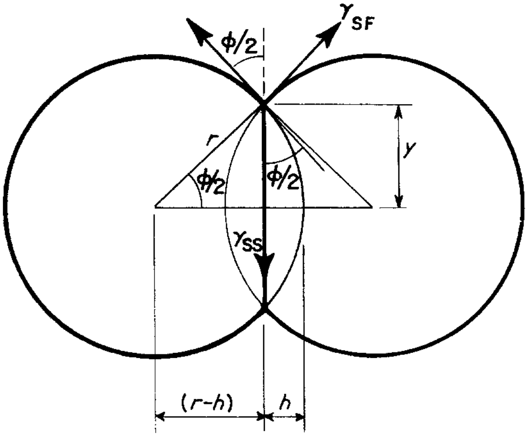

Figure 1 Representation of spherical particles in an ideal two phase, two particle system, showing the formation of the dihedral angle, ϕ.

Equation 1 can be derived by either a mechanical or thermodynamic approach. The mechanical approach consists of a balance of three forces at equilibrium as deduced from Fig. 1. The thermodynamic or energetic approach, however, is less straightforward, which to the authors' knowledge, has not yet been reported in the literature. This approach provides a basic understanding for the formation of the equilibrium configuration. Therefore, the present objective is to present a thermodynamic solution of Equation 1.

The basic assumptions for the model shown in Fig. 1 are that the particles, S, are of equal size with isotropic surface energies and the lowest free energy configuration, that is, they are spheres. The model further assumes that as the spheres interpenetrate an isotropic grain boundary forms and grows, and that the displaced materials, represented by h in Fig. 1, are uniformly distributed over the free surfaces in order to maintain the lowest free energy configuration of the spheres at all times. The differential change of Gibbs free energy for the entire system at a given time, δG_{sys}, can then be represented by

$$\delta G_{\mathrm{sys}} = \delta \int_{A_{SS}}^{\gamma_{SS}} \mathrm{d}A_{SS} + \delta \int_{A_{SF}}^{\gamma_{SF}} \mathrm{d}A_{SF}, \qquad (2)$$

where A_{SS} and A_{SF} are areas of solid–solid and solid–fluid interfaces, respectively. The first term on the right is positive and the second, negative. As long as δG_{sys} remains negative, the interpenetration of the two spherical particles (increase of A_{SS}) continues. When δG_{sys} becomes zero, the system reaches a metastable equilibrium state. This system with the indicated boundary conditions does not reach the lowest free energy configuration of a single sphere since further interpenetration results in a positive value of δG_{sys}.

The thermodynamic approach may now be followed for the derivation of Equation 1 for the equilibrium configuration. A material balance for each spherical particle requires that

$$\rho V_{\mathrm{i}} = \rho(V_{\mathrm{t}} - V_{\mathrm{cap}}), \qquad (3)$$

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*Although they are not exactly equal, interfacial energies and tensions are used interchangeably.

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where V_i is the initial volume of each spherical particle, V_t is the transient increasing volume of each interpenetrating spherical particle at a given instant and V_{cap} is the volume of the resulting cap removed from each particle. The density of the solid is ρ.

Differentiation of Equation 3 results in $\mathrm{d}V_t - \mathrm{d}V_{\mathrm{cap}} = 0$, or $4r^2\mathrm{d}r - 2rh\mathrm{d}h - h^2\mathrm{d}r + h^2\mathrm{d}h = 0$, or

$$\mathrm{d}r = \left(\frac{h\mathrm{d}h}{2r+h}\right), \tag{4}$$

where r is the radius of the spherical particle with a volume V_t, and h is the height of the cap removed.

If A = the surface area of each spherical particle with a volume V_t, A_1 = the curved surface area of the cap, and A_2 = the base area of the cap, then

$$A = 4\pi r^2 \tag{5}$$

$$A_1 = 2\pi rh \tag{6}$$

$$\begin{aligned} A_2 &= \pi y^2 = \pi[r^2 - (r-h)^2] \\ &= \pi(2rh - h^2). \end{aligned} \tag{7}$$

Differentiation of Equations 5, 6 and 7 results in

$$\mathrm{d}A = 8\pi r\mathrm{d}r \tag{8}$$

$$\mathrm{d}A_1 = 2\pi r\mathrm{d}h + 2\pi h\mathrm{d}r \tag{9}$$

$$\mathrm{d}A_2 = 2\pi r\mathrm{d}h + 2\pi h\mathrm{d}r - 2\pi h\mathrm{d}h \tag{10}$$

From Equation 2, and Fig. 1

$$\begin{aligned} \delta G_{\text{one sphere}} &= \delta \int_{A_{\mathrm{SS}}=A_2}^{\gamma_{\mathrm{SS}}/2^*} \mathrm{d}A_2 \\ &\quad + \delta \int_{A_{\mathrm{SF}}=A-A_1}^{\gamma_{\mathrm{SF}}} (\mathrm{d}A - \mathrm{d}A_1). \end{aligned} \tag{11}$$

Substituting Equations 8, 9 and 10 in Equation 11 gives

$$\begin{aligned} \delta G_{\text{one sphere}} &= \pi\Big[-\delta \int \gamma_{\mathrm{SS}}(h\mathrm{d}h - h\mathrm{d}r - r\mathrm{d}h) \\ &\quad + 2\delta \int \gamma_{\mathrm{SF}}(4r\mathrm{d}r - r\mathrm{d}h - h\mathrm{d}r)\Big]. \end{aligned} \tag{12}$$

Substituting Equation 4 into Equation 12 produces

$$\begin{aligned} \delta G_{\text{one sphere}} &= \pi\left[\delta \int \frac{\gamma_{\mathrm{SS}}(rh\mathrm{d}h - 2r^2\mathrm{d}h)}{2r+h}\right. \\ &\quad \left. + 2\delta \int \frac{\gamma_{\mathrm{SF}}(3rh\mathrm{d}h - 2r^2\mathrm{d}h - h^2\mathrm{d}h}{2r+h}\right]. \end{aligned} \tag{13}$$

At equilibrium, $\delta G_{\text{one sphere}} = 0$. Equation 13 then becomes

$$\frac{\gamma_{\mathrm{SS}}}{2\gamma_{\mathrm{SF}}} = \frac{-(2r-h)(r-h)}{r(h-2r)} = \frac{r-h}{r} = \cos\frac{\phi}{2}, \tag{14}$$

or

$$\gamma_{\mathrm{SS}} = 2\gamma_{\mathrm{SF}} \cos\frac{\phi}{2}$$

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BOON WONG*
JOSEPH A. PASK
Materials and Molecular Research Division,
Lawrence Berkeley Laboratory and
Department of Materials Science and
Mineral Engineering,
University of California,
CA 94720, USA

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*Present address: Spectrolab Inc., 1250 Gladstone Ave, Sylmar, CA 91342, USA