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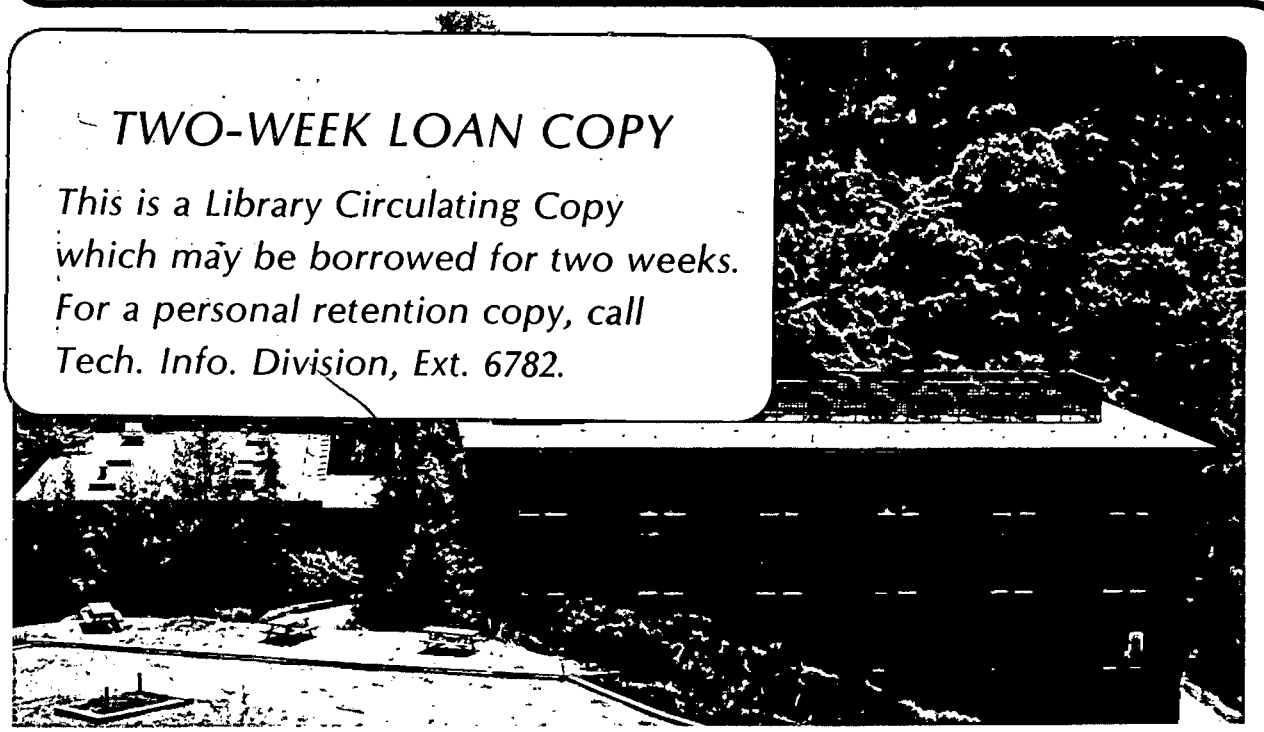

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ABSTRACT

A model based on two interpenetrating spheres forming a solid/solid interface is used to derive the familiar dihedral angle equation $\gamma_{SS} = 2\,\gamma_{SF}\cos\frac{\phi}{2}$ thermodynamically. The equilibrium dihedral angle corresponds to one when the incremental increase of the total solid/solid interfacial energy is equal to the incremental decrease of the total solid/fluid interfacial (surface) energy, i.e. when an incremental interfacial free energy change for the system is zero.

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

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

where γ_{SS} is the specific interfacial energy* at solid/solid interface, i.e. grain boundary energy, and γ_{SF} is the specific interfacial energy at solid/fluid (vapor or liquid) interface. (In real systems dihedral angles would be achieved but symmetrical configurations would practically never be reached because of the anisotropy of 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.)

Equation (1) can be derived by two alternative approaches, namely mechanical and thermodynamic. The mechanical approach consists of a balance of

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

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 Eq. (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, i.e. 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 are uniformly distributed over the free surfaces in order to maintain the lowest free energy configuration of spheres at all times. The differential change of Gibbs free energy, δG_{sys}, for the entire system at a given time can then be represented by

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

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 δG_{sys}.

We can now follow the thermodynamic approach for the derivation of Eq. (1) for the equilibrium configuration. A material balance for each spherical particle requires that

$$\rho V_i = \rho(V_t - V_{cap}) \tag{3}$$

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 Eq. (3) results in $dV_t - dV_{cap} = 0$, or $4r^2dr - 2rhdh - h^2dr + h^2dh = 0$, or

$$dr = \left(\frac{hdh}{2r+h}\right) \tag{4}$$

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

Let 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

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

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

$$A_2 = \pi y^2 = \pi\left(r^2-(r-h)^2\right) = \pi(2rh-h^2) \tag{7}$$

Differentiation of Eqs. (5), (6) and (7) results in

$$dA = 8\pi r dr \tag{8}$$

$$dA_1 = 2\pi r dh + 2\pi h dr \tag{9}$$

$$dA_2 = 2\pi r dh + 2\pi h dr - 2\pi h dh \tag{10}$$

From Eq. (2) and the figure

$$\delta G_{\text{one sphere}} = \delta \int_{A_{SS}=A_2} \frac{\gamma_{SS}}{2^*}\, dA_2 + \delta \int_{A_{SF}=A-A_1} \gamma_{SF}(dA-dA_1) \tag{11}$$

Substituting Eqs. (8), (9) and (10) into Eq. (11),

$$\delta G_{\text{one sphere}} = \pi\left[-\delta\int\gamma_{SS}(hdh-hdr-rdh) + 2\delta\int\gamma_{SF}(4rdr-rdh-hdr)\right] \tag{12}$$

Substituting Eq. (4) into Eq. (12),

$$\delta G_{\text{one sphere}} = \pi\left[\delta\int\frac{\gamma_{SS}(rhdh - 2r^2dh)}{2r + h} + 2\delta\int\frac{\gamma_{SF}(3rhdh - 2r^2dh - h^2dh}{2r + h}\right] \tag{13}$$

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

$$\frac{\gamma_{SS}}{2\gamma_{SF}} = \frac{-(2r - h)(r - h)}{r(h - 2r)} = \frac{r - h}{r} = \cos\frac{\phi}{2}\ , \text{ or}$$

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

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*A factor of 1/2 is introduced because each base of the cap is assumed to be equally shared by the two spheres (Fig. 2).

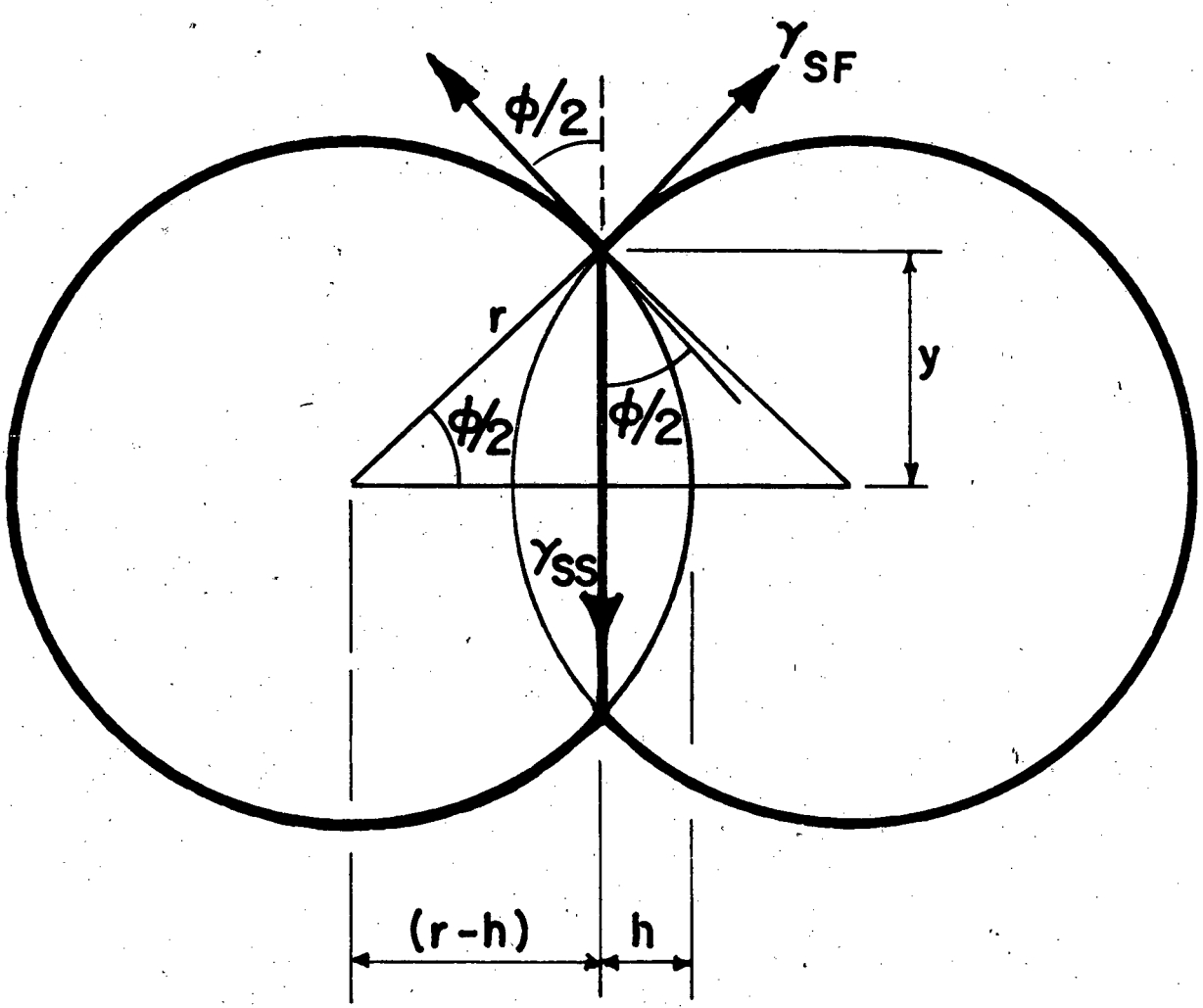

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Fig. 1

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