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CALCULATION OF SOLID LIQUID SURFACE ENERGY FOR PURE MATERIALS AND BINARY ALLOYS

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SUMMARY

In this work, basic concepts (Gibbs free energy, equilibrium, driving force, undercoolings) for the solid-liquid phase transformation have been briefly mentioned. Solid-liquid Surface energy σ_{sL} has been obtained for pure materials and binary alloy systems. The effect of the crystallographic orientation and nonspherical curvature effect on σ_{sL} have been also discussed.

SAF MADDELER VE İKİLİ ALAŞIMLAR İÇİN KATI-SIVI YÜZEY ENERJİSİNİN HESAPLANMASI

ÖZET

Bu çalışmada, katı-sıvı faz dönüşümünün temel kavramları (Gibbs serbest enerjisi, denge, itici güç, aşırısoğumalar) üzerinde kısaca durulmuştur. Saf maddeler ve ikili alaşımlar için katı-sıvı yüzey enerjisi σ_{sL} elde edilmiştir. σ_{sL} üzerine kristalografik yönelme ve küresel olmayan eğriliğin etkisi ayrıca tartışılmıştır.

1- INTRODUCTION

The solid-liquid surface energy is an important factor in solidification theory, nucleation theory, thermodynamics and solid-liquid phase transformation and is one of the basic physical constants (such as density, conductivity, entropy, resistivity, melting temperature etc.) for materials. Solid-liquid surface energy, σ_{sL} is difined as the work done to produce unit area of surface at the solid-liquid interface.When the σ_{sL} energy is isotropic, it is numerically equal to the solid-liquid surface tension per unit length if expressed in similar units [1,2] . In order to understand solid-liquid phase transformations and to obtain solid-liquid surface energy it is necessary to undarstand, Gibbs free energy, equilibrium, driving force, and undercoolings.

2- THE GIBBS FREE ENERGY and EQUILIBRIUM

The Gibbs free energy G, is defined as

$$G = H - TS \qquad (1)$$

where T is the absolute temperature, S is the entropy (measure of the randomness of the system) and H is the enthalpy (measure of the heat content of the system). H is defined as

$$H = E + PV \qquad (2)$$

where P is the pressure, V is the volume and E is the internal energy of the system. Internal energy arises from the increase of the total kinetic and potential energies of the atoms within the system. When dealing with solid and liquid phases, the PV term is usually very small in comparison to E, that is $H \simeq E$.

In classical thermodynamics a closed system is said to be in equilibrium when it has its lowest possible value of the Gibbs free energy at constant pressure and temperature, i.e.

$$(dG)_{T,P} = 0 \qquad (3)$$

As can be seen from fig.1 , equation (3) is satisfied at states A and B for the system. However, A lies at a local minimum in free energy but does not have the lowest possible free energy, G, of the system. Such states are called metastable equilibrium states to distinguish them from the stable equilibrium state. When the initial state of a system has a higher Gibbs free energy, G_1, then the final state G_2, i.e. $\Delta G = G_2 - G_1 < 0$ phase transformation occurs. The phase transformation occurs because the initial state of a system is less stable than the final state. For discussion of the solid-liquid phase transformation and the equilibrium at the interface it would be useful to look at the variation of G with T. This can be obtained from the following result of classical thermodynamics. For a system of fixed mass and compositior

$$dG = - SdT + VdP \quad \text{at constant pressure } dP = 0 \text{ and} \qquad (4)$$

$$\left(\frac{aG}{aT}\right)_P = -S \qquad (5)$$

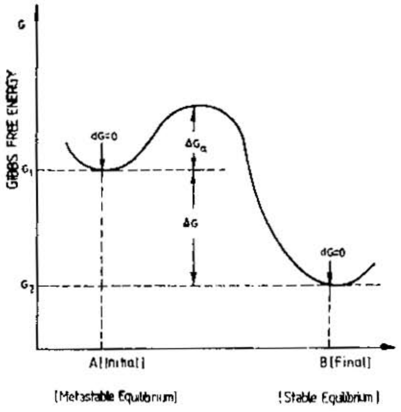


Fig.1.1 Transformation from initial to final state of a system

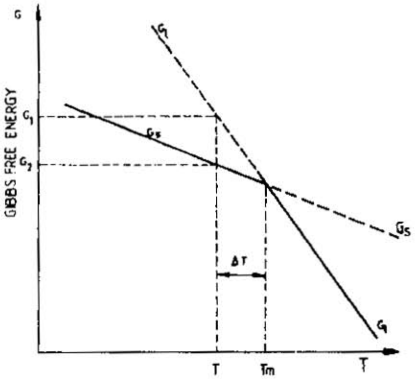
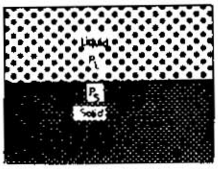
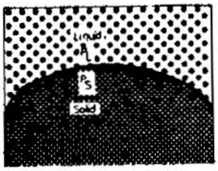


Fig.1.2 Gibbs free energy for solid and liquid phases as a function of temperature near the equilibrium melting point T_m. (the curvature of the G_s and G_L lines has been neglected)



a) Planar S-L Interface $P_s = P_l$



b) Curved S-L Interface $P_s > P_l$

Fig.3 Pressures, S-L interface relation (S and L refer to solid and liquid respectively)

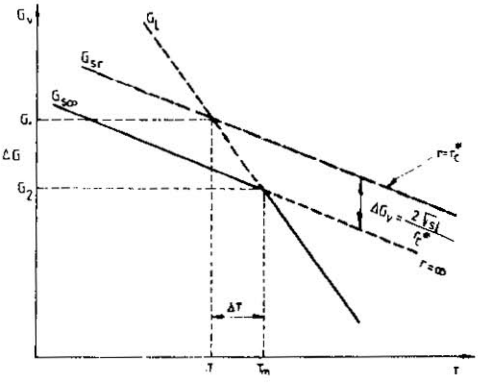


Fig.4 Volume free energy as a function of temperature for solid and liquid phases, showing the origin of the curvature effect

This means when a pure solid or pure liquid is heated up the Gibbs free energy decreases. As can be seen from fig.2 the liquid free energy decreases more rapidly than the solid free energy because of the larger entropy $[(aG/aT)_p = - S]$ of the liquid phase. For temperatures up to T_m the solid phase has a lower free energy and thus is the stable equilibrium phase; whereas above T_m the liquid phase has the lower free energy and is thus the equilibrium state of the system. At the melting point the free energies of both phases are the same, so that the two phases can co-exist in equilibrium. If a liquid is undercooled by ΔT below its equilibrium melting temperature, T_m, it might be expected that the liquid should transform spontaneously to solid. However, this does not often occur. For example under suitable conditions pure materials can be supercooled from a few ^oC to over 300^oC before solid forms spontaneously [3,4] . In order for a liquid to transform to the solid phase at some temperature ΔT below T_m, a small number of atoms or molecules in the liquid must come together to form embryos or groups of atoms having solid like structures. As shown in fig.2 the Gibbs free energy decreases for the solid-liquid phase transformation and this free energy decrease provides the driving force for the solidification.

3- DRIVING FORCE

The magnitude of the free energy decrease (change) for the solidification can be obtained as follows;

Assuming G_S and G_L lines near T_m are straight lines (fig.2), H_S, H_L, $(aG_S/aT)_P$ and $(aG_L/aT)_P$ do not vary with the temperature over the range of temperatures from $T_m - \Delta T$ to T_m. Then the Gibbs free energy for liquid and solid can be written as

$$G_L = H_L - TS_L, \qquad G_S = H_S - TS_S \tag{6}$$

or

$$\Delta G = G_S - G_L = H_S - H_L - T\,(S_S - S_L) = \Delta H - T\,\Delta S \tag{7}$$

At the equilibrium temperature, T_m, $G_L = G_S$ thus $\Delta G = 0$. Therefore

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} \tag{8}$$

where L is the latent heat of fusion. Consequently the decrease of the free energy can be expressed as

$$\Delta G \approx L - \frac{LT}{T_m} = \frac{L\,\Delta T}{T_m} = \Delta T\,\Delta S \tag{9}$$

This equation gives the energy change which is the thermodynamic driving force for solidification. Solidification, that is, transformation of a material from the liquid state to the solid state (i.e. freezing) does not happen at the equilibrium melting temperature, T_e but at a temperature below this temperature, T_1 . The reason for this is that, when the first solid forms, a large amount of energy is needed to form a new solid-liquid interface. The temperature difterence between T_e and T_1 is known as undercooling which is given as [5]

$$T_e - T_1 = \Delta T = \Delta T_k + \Delta T_d + \Delta T_r \tag{10}$$

4- UNDERCOOLING

4.1- Kinetic Undercooling, ΔT_k

In all materials there is an energy barrier to the transfer of atoms from the liquid to the solid phase and vice versa. Growth of solid only takes place if atoms jump more frequently from the liquid to the solid phase and this can only occur if the interface is cooled below its equilibrium temperature. It is this undercooling, necessary to drive the transfer of atoms which is known as the kinetic undercooling. If atoms jump more frequently from the solid to the liquid phase, the liquid phase grows, (melting occurs). If addition of the atoms is exactly balanced by the rate of dissolution then the system is said to be at equilibrium. From this definition, $\Delta T_k=0$ (At the equilibrium condition for pure and multi-component systems)

4.2- Diffusion Undercooling, ΔT_d

Diffusion undercooling occurs because of the composition gradient in the liquid phase and this can be expressed az;

$$\Delta T_d = m(C_{L\infty} - C_{Lr}) \tag{11}$$

where $C_{L\infty}$ is the liquid composition at the planar solid-liquid interface, C_{Lr} is the liquid composition at the curved interface and m is the liquidus necessary to define chemical potential (partial molar free energy). Generally speaking chemical potential is the change in free energy of the whole system, i.e.

$$\mu_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{T_j P_j n_j} \qquad (12)$$

where i and j refer to different components.

Regarding the properties of the bulk phases,[6] in a one-component system chemical potential of the species i equals the increase in the value of G for the system resulting from the addition of one mole of i at constant T and P. That is $\Delta G = \mu_i$ and as the increase in the value of G of the one component system is simply the molar free energy of i then

$$g_i = \mu_i \qquad (13)$$

Assume that a curved interface is in metastable equilibrium with its surrounding. The chemical potential of each phase is then made equal on both sides of the interface that is

$$\mu_{isr} = \mu_{iL\infty} \qquad (\mu_{iLr} = \mu_{iL\infty}) \qquad (14)$$

The pressure inside a curved surface will always be greater than that outside due to the tension in the surface (fig.3). Considering just mechanical equilibrium that is no transfer of metarial

$$(P_S - P_L)\, dV = \sigma_{sL}\, d\varphi \qquad (15)$$

where P is the pressure, S and L refer to solid and liquid respectively, dV and d φ volume and surface area change due to the curvature effet.

Assuming the curved surface is a sphere, (i.e.: $\frac{d\varphi}{dV} = \frac{2}{r}$ [14])

$$\Delta P = \frac{2\sigma_{sL}}{r} \qquad (16)$$

5.1- Solid-liquid Surface Energy For Pure Materials

The molar volume of a pure material can be expressed using equation (13) as slope (which is negative when $k<1$). Where k; is the distribution coefficient

As can be seen from equation (11) ΔT_d is always zero for pure materials. If multicomponent systems are at their equilibrium conditions the composition of the solid and liquid phases will be homogeneous so thus the composition gradient will be zero. Therefore, from equation (11)

$\Delta T_d = 0$ (only at the equilibrium condition for multicomponent systems)
$\Delta T_d = 0$ (always for pure materials)

Consequently at equilibrium, total undercooling is equal to the curvature undercooling. In mathematical terms, from equation (10)

$\Delta T = \Delta T_r$ (at the equilibrium condition for pure, and multicomponent systems)

4.3- The Curvature Undercooling, ΔT_r

This is commonly known as the Gibbs-Thomson effect and arises from the fact that there is a surface energy associated with a solid-liquid interface. Solid - liquid surface energy, σ_{sL}, related to the curvature undercooling, ΔT_r, can be deduced by combining the condition of mechanical equilibrium of a equilibrated curved interface and the condition of chemical equilibrium. In the following sections, ΔT_r, σ_{sL} are going to be obtained for pure materials and two-component systems. The effect of crystallographic orientation and nonspherical curvature effect on ΔT_r are also going to be discussed. Finally a general curvature undercooling equation which allows σ_{sL} to be calculated for binary alloys is going to be obtained relating to the radii of the curvatures r_1, r_2, and the weighted entropy of fusion ΔS^*.

5- DETERMINATION OF SOLID-LIQUID SURFACE ENERGY, σ_{sL}

When the solid-liquid interface is curved, there is an additional energy term, σ_{sL} which cannot be neglected. An equation, relating to curvature undercooling can be deduced for this additional energy term, σ_{sL}, by combining the condition of mechanical equilibrium of a curved interface and the condition of chemical equilibrium.

To understand chemical equilibrium and to derive the equation for σ_{sL} it is

$$\left(\frac{ag}{aP}\right)_T = \left(\frac{a\mu}{aP}\right)_T = V \qquad (17)$$

For a pure material the molar free energy change (i.e. driving force) between the phases can be expressed using equations (16) and (17) as follows (for an incompressible solid):

$$\Delta g = g_{sr} - g_{L\infty} = \int_{P_L}^{P_s} VdP \qquad (18a)$$

$$\Delta g = \Delta PV \qquad \Delta g = \frac{2\,\sigma_{sL}}{r}\,V \qquad (18b)$$

From equation (9) or after the geometry of fig.4

$$\Delta g = \Delta T_r\,\Delta S \quad \{\,\Delta g = g_{sr} - g_{L\infty} = -\Delta T\left[\left(\frac{ag}{aT}\right)_s - \left(\frac{ag}{aT}\right)_L\right] = \Delta T_r \Delta S\,\} \qquad (18c)$$

Then the curvature undercooling related to the solid-liquid surface energy for pure materials can be expressed from equation (18b) and (18c) as follows;

$$\Delta T_r = \frac{2\,\sigma_{sL}}{r\,\Delta S}\,V_s \qquad (19)$$

5.2- Solid-liquid Surface Energy For Binary Alloys

For an alloy the choice of a term to use for the thermodynamic driving force ΔG_v is not so obvious because the Gibbs free energy is not simple as for pure materials, it is a function of the composition for both the solid and liquid phases (fig.5). The important condition for the equilibrium of an alloy is that the chemical potential must everywhere have the same value as well as the fact $T_s = T_L$ at the solid-liquid interface.

In an A-B alloy the molar free energy can be written as

$$g = n_A\,\mu_A + n_B\,\mu_B \qquad (20)$$

where n_A and n_B are the number of atoms and μ_A and μ_B are the chemical potentials for components A and B respectively.

The effect of the curved surface for a binary alloy may be illustrated on a free energy composition diagram as shown in fig.5b. This diagram is a plot of the average free energy per atom $\bar{g}_{s\infty}$, $\bar{g}_{L\infty}$ and $\bar{g}_{sr}$ against composition. As can be seen from fig.5 the chemical potential of a phase is given by the intercept on the A and B axes of a tangential line to the free energy curve for the composition concerned. Thus for two phases to be in equilibrium, they must have a common tangential line. That is for a planar interface $\mu^A_{s\infty} = \mu^A_{L\infty}$ and $\mu^B_{s\infty} = \mu^B_{L\infty}$ for compositions $C_{s\infty}$ and $C_{L\infty}$. As can be seen from fig.5b the $g_{s\infty}$ curve is shifted up at constant composition to allow for the curved surface to be in metastable equilibrium with the surroundings. Metastable equilibrium occurs when the new plot has a common tangential line with the liquid line. Thus ensuring that $\mu^A_{sr} = \mu^A_{Lr}$ and $\mu^B_{sr} = \mu^B_{Lr}$ for the compositions C_{sr} and C_{Lr} .

The corresponding molar free energy change (i.e. driving force) due to the curvature effect for a spherical incompressible solid of constant composition can be expressed as follows:

From equation (20)

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_B} = n_A\left(\frac{\partial \mu}{\partial P}\right)_{T,n_A,n_B} + n_B\left(\frac{\partial \mu^B}{\partial P}\right)_{T,n_A,n_B} \qquad (21a)$$

where $\left(\frac{\partial \mu^A_s}{\partial P}\right)_{T,n_A,n_B} = V^A_s$ $\left(\frac{\partial \mu^A_s}{\partial P}\right)_{T,n_A,n_B} = V_s$ the partial atomic volumes of the components A and B respectively.

The free energy change can be written from equation (21a) as

$$\Delta g = n_A\int_{P_L}^{P_s} V_s \, dP + n_B\int_{P_L}^{P_s} V_s \, dP \quad \text{that is } \Delta g = (n_A V^A_S + n_B V^B_S)\,\Delta P \qquad (21b)$$

Thus from equation (16) (for an incompressible spherical solid)

$$\Delta g = \frac{2\sigma_{sL}}{r} V_s \qquad \text{where } V_s = n_A V^A_S + n_B V^B_S \qquad (21c)$$

As can be seen from the geometry of fig.5b a relation between Δg and ΔC_L and from fig.6 a relation between ΔC_L and ΔT_r can be obtained. Therefore, ΔT_r may be expressed as a function of composition of both phases, liquidus slope, m_L , equilibrium temperature, T, principal radius, r, and solid-liquid surface energy, σ_{sL} .

From the geometry of fig.5b $\Delta C_L = C_{Lr} - C_{L\infty}$

ΔC_L is usually of small magnitude and so to a good approximation [7](from similar triangles, ΔMNQ similar to ΔRSQ)

$$\frac{\mu^A_{sr} - \mu^A_{s\infty}}{\bar{g}_{sr} - \bar{g}_{s\infty}} = \frac{\Delta G}{\Delta g} = \frac{1 - C_{L\infty}}{C_{s\infty} - C_{L\infty}} \tag{22a}$$

In terms of the activation coefficients (at constant temperature and pressure) Δ G is given as [7]

$$\Delta G = \Delta\mu = kTLn \left(\frac{\gamma_{Lr} C_{Lr}}{\gamma_{L\infty} C_{L\infty}}\right) \tag{22b}$$

Assuming that the activation coefficients γ_{Lr} and $\gamma_{L\infty}$ are constant for the range of composition considered. Therefore

$$Ln\left(\frac{C_{Lr}}{C_{L\infty}}\right) = Ln\left(1 + \frac{\Delta C_L}{C_{L\infty}}\right) \cong \frac{\Delta C_L}{C_{L\infty}} \quad \text{that is} \quad \Delta G = kT \frac{\Delta C_{L\infty}}{C_{L\infty}} \tag{22.c}$$

Equations (21.c), (22.a) and (22.c) thus give

$$\Delta C_L = \frac{2\sigma_{sL}}{rkT} V_s \frac{(1 - C_{L\infty}) C_{L\infty}}{(C_{s\infty} - C_{L\infty})} \tag{23}$$

For small changes it is useful to note that ΔC_L is related to ΔT_r by the liquidus slope, m, (fig.6). That is $m \Delta C_L = \Delta T_r$. So that the curvature undercooling can be related to composition of the phases, liquidus slope, equilibrium temperature, principal radius and solid-liquid surface energy by

$$\Delta T_r = \frac{2\sigma_{sL} m V_s}{rkT} \frac{(1 - C_{L\infty})}{(C_{s\infty} - C_{L\infty})} C_{L\infty} \tag{24}$$

The atomic molar free energy change $\bar{g}_{sr} - \bar{g}_{s\infty} = \Delta g = \frac{2\sigma_{sr}}{r} V_s$ is valid even when the composition and the temperature simultaneously change with the principal curvature. This molar free energy change can be expressed as [14]

$$\bar{g}_{sr} - \bar{g}_{s\infty} = \Delta g = \frac{2\sigma_{sL}}{r} V_s = \int_{T_\infty}^{Tr} \Delta S^* dT + kT_\infty \Delta C_L \frac{(C_{s\infty} - C_{L\infty})}{(1 - C_{L\infty}) C_{L\infty}} \tag{25}$$

where $\Delta S^* = [(1 - C_{s\infty})(S^A_s - S^A_L) + C_{s\infty}(S^B_s - S^B_L)]$ is the weighted entropy

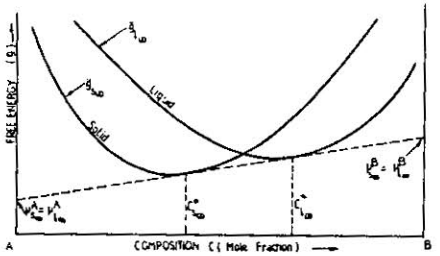


Fig.5a Free energy versus composition for binary alloy at constant temperature (after ref.19)

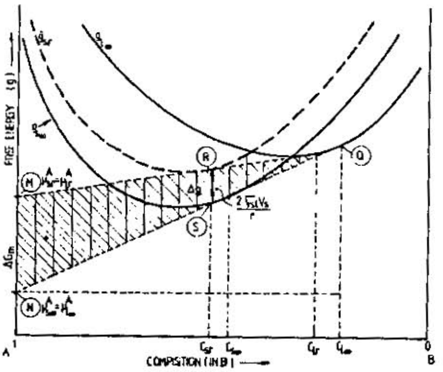


Fig.5b To illustrate the Gibbs-Thomson (curvature) effect for a binary alloy at constant temperature (after ref. 7)

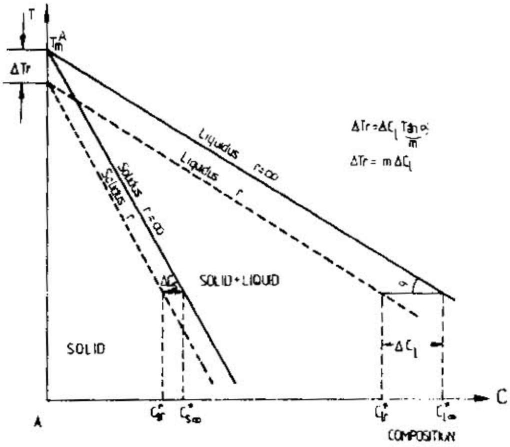


Fig.6: Depression of equilibrium liquidus and solidus of a binary alloy system because of the Gibbs-Thomson effect.

change $V_s = (1 - C_{s\infty})V_s^A + C_{s\infty}V_s^B$ is the atomic volume of the solid. k is Boltzmann's constant, T_∞ , T_r are the equilibrium and the curved interface temperatures respectively. ΔC_L is the composition difference in the liquid phase at the interface because of the curvature effect (fig.6). The change in the liquid composition with radius r at constant temperature from equation (25) is thus

$$\Delta C_L = \frac{2\sigma_{sL}}{rkT} V_s \frac{(1 - C_{L\infty})C_{L\infty}}{(C_{s\infty} - C_{L\infty})} \qquad (26)$$

which is exactly the same as equation (23).

Assuming that ΔS^* is reasonably constant over the temperature range considered, thus the change in the temperature at constant composition (i.e. $\Delta C_L = 0$)

[from equation (25)] is given by

$$\Delta T_r = \frac{2\,\sigma_{sL}}{r\,\Delta S^*}\,V_s = \frac{2\sigma_{sL}}{r\,\Delta S_f^*} \qquad (27)$$

where $\Delta S_f^* = \left(\frac{\Delta S^*}{\Delta V_s}\right)$ entropy of fusion per unit volume which is of identical form to that obtained for the pure materials (equation 19). The curvature undercooling equations (related to solid-liquid surface energy σ_{sL}) can also be obtained by homogeneous nucleation theory [8] . Either equation(24) or equation (27) may be used to calculate the solid-liquid surface energy, σ_{sL} , for binary alloys.

So far the curvature undercooling equations (so thus σ_{sL}) have been obtained and discussed for the spherical solid-liquid surface and isotropic σ_{sL} for pure materials and binary alloys. It was thought that it would be useful to discuss

Non-spherical surface effect on ΔT_r , (σ_{sL}) and
The crystallographic orientation effect on σ_{sL} , (ΔT_r)

6- THE GIBBS-THOMSON EQUATION FOR NON-SPHERICAL SURFACES [9]

So far in the discussion spherical surfaces have been considered. Now the treatments are going to be extended to non-spherical surfaces. As mentioned in introduction the surface energy is the work done in creating unit area of new surface and is thus numerically equal to the surface tension σ_{sL} (force per unit length).

Considering unit length of the segment $\delta\theta$ of a cylindrical surface shown in fig.7a. There is an inward force, F_1, due to the surface tension of $2\sigma_{sL}\sin\left(\frac{\theta}{2}\right)$ and this must be equal to the outward force, F_2 ;$r\,\Delta P\,\delta\theta$, due to the pressure difference across the surface so that as $\delta\theta \to 0$

$$\sigma_{sL}\delta\theta = \Delta P r\,\delta\theta \qquad \text{or} \qquad \Delta P = \frac{\sigma_{sL}}{r} \qquad (28)$$

Now considering curvature in two directions (fig.7b) where r_1 and r_2 are the principal radii of curvature. The two pressure differences will be added so that

$$\Delta P = \sigma_{sL}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (29)$$

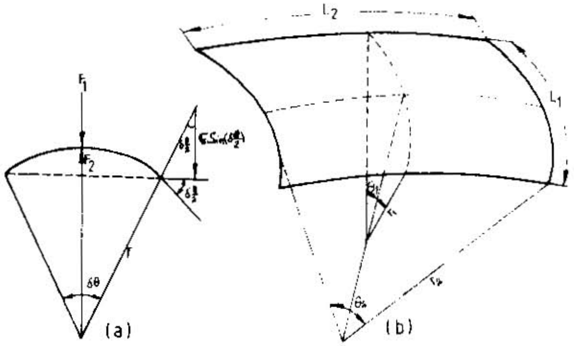


Fig.7 Diagrams used in calculation of the Gibbs-Thomson equation for non-spherical surfaces

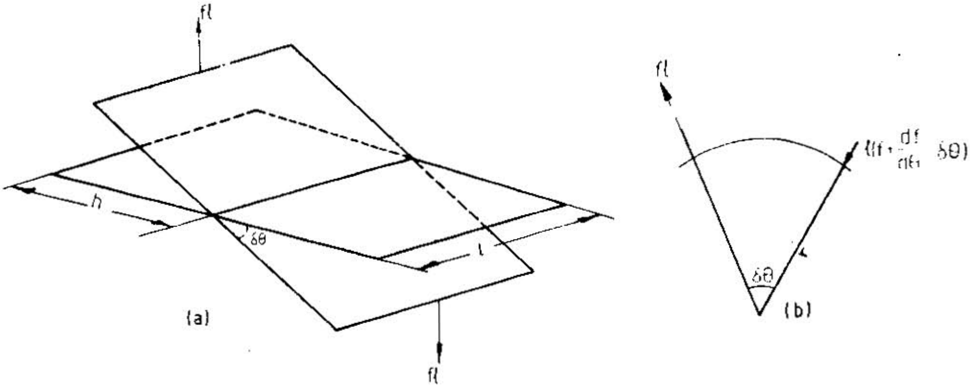


Fig.8 Diagrams used in calculation of the crystallographic orientation effect on σ_{sL}

Thus the increase in the chemical potential (equation 18b)

$$\mu_{sr} - \mu_{s\infty} = V_s\, \Delta P \qquad \text{i.e.} \qquad \Delta P = \sigma_{sL}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)V_s \qquad (30)$$

That is $\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$ replaces $\frac{2}{r}$ in equations (19, 23, 25,27) obtained for the curvature undercooling when the solid-liquid surface is non-spherical.

7- CRYSTALLOGRAPHIC ORIENTATION EFFECT ON SURFACE ENERGY σ_{sL} [10,11]

In the previous discussions it has been assumed that the surface energy (energy per unit area) or surface tension (force per unit length) was identical to the surface stress and that the surface stress did not vary with orientation [12,13]. These quantities are numerically equal when atomic mobilities are sufficiently high to preserve the microscopic configuration of the surface following the deformation. For a solid phase due to the long range correlation in atomic positions and low atomic mobilities, it may not be possible in any reasonable experimental time to keep constant the local configuration around any particular atom in the surface region where the deformation of the surface area is performed. Hence in this case surface tension will be dependant on the crystallographic orientation. Still even if σ_{sL} is a function of the crystallographic orientation, a general curvature undercooling equation relating to σ_{sL} can be obtained.

When σ_{sL} is a function of orientation a couple will be needed to prevent a flat surface rotating to a lower energy position, fig.8a. The work done against the couple is

$$W_1 = 2f\ell h\,\delta\theta \tag{31}$$

where f is the force per unit length. (For description of h, ℓ, δ see fig.8)

For equilibrium W_1 must be equal to the change in free energy of the surface

$$W_2 = 2h\ell\frac{d\,\sigma_{sL}}{d\,\theta}\,\delta\theta \tag{32}$$

From equations (31) and (32)

$$f = \frac{d\,\sigma_{sL}}{d\,\theta} \tag{33}$$

Clearly, although there is a couple there is no net vertical force on the flat surfaces of fig.8a. For a curved surface however the inward force,, $f\ell$ on one side is not equalto the outward force on the other $\ell\,(f+\frac{df}{d\theta}\,\delta\,\theta)$ (see fig.8b). So that there is a net inward force

$$\Delta f = \frac{\ell df}{d\theta}\,\delta\theta = \frac{d^2\sigma_{sL}}{d\theta^2}\,\delta\theta \tag{34}$$

This inward force must be added to that arising from the surface tension. So equation (27) becomes

$$\Delta P\ell r\delta\,\theta = \sigma_{sL}\ell\delta\,\theta + \frac{\ell d^2\sigma_{sL}}{d\,\theta^2}\,\delta\theta \quad \text{or} \quad \Delta P = \frac{1}{r}\,(\sigma_{sL} + \frac{d^2\sigma}{d\,\theta^2}) \tag{35}$$

Considering the curvature in two directions (fig.7b) gives

$$\Delta P = \frac{1}{r_1}\,(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_1^2}) + \frac{1}{r_2}\,(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_2^2}) \tag{36}$$

so that from equations (28) and (29)

$$\mu_{sr} - \mu_{s\infty} = \Delta g = V_s \left[\frac{1}{r_1} \left(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_1^2} \right) + \frac{1}{r_2} \left(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_2^2} \right) \right] \tag{37}$$

If this $\mu_{sr} - \mu_{s\infty}$ value is used in equation (24), ΔT_r is obtained (for constant temperature) as

$$\Delta T_r = \left[\frac{1}{r_1} \left(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_1^2} \right) + \frac{1}{r_2} \left(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_2^2} \right) \right] \frac{mV_s}{kT} \frac{(1-C_{L\infty})C_{L\infty}}{(C_{s\infty}-C_{L\infty})} \tag{38}$$

or (for constant composition)

$$\Delta T_r = \left[\frac{1}{r_1} \left(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_1^2} \right) + \frac{1}{r_2} \left(\sigma_{sL} + \frac{d^2\sigma_{sL}}{d\,\theta_2^2} \right) \right] \frac{V_s}{\Delta S^*} \tag{39}$$

As can be seen easily when σ_{sL} is not a function of the crystallographic orientation i.e. isotropic, equation (38) and equation (39) become (for the non-spherical surface)

$$\Delta T_r = \frac{\sigma_{sL}\, mV_s}{kT} \frac{(1-C_{L\infty})C_{L\infty}}{(C_{s\infty}-C_{L\infty})} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \tag{40}$$

$$\Delta T_r = \frac{\sigma_{sL} V_s}{\Delta S^*} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \tag{41}$$

When $r_1 = r_2$ i.e: solid-liquid surface is spherical, equations (40) and (41) become equations (24) and (27) respectively.

8- CONCLUSION

Equation (41) is the form of the Gibbs-Thomson relation which is most useful for the application of the solid-liquid interface in solidification and melting as it expresses the effective change in melting point at a curved interface, and it is the most powerful method at present available for measuring solid-liquid surface nergy experimentally, for the equilibrated solid-liquid interface. For a binary alloy system when the solid-liquid interface is at equilibrium, the solid and the liquid phase will be uniform, so thus composition difference in the phases will be negligible or zero.

The Gibbs-Thomson relation (the equation (41))has been successfully used to measure solid-liquid surface energies for transparent organic materials by

Jones and Chadwick [15], Schaefer et al [16] and Hardy [17] , and for binary metalic alloys by Gündüz and Hunt [18] . In conclusion the equation (41) can be used to calculate σ_{sL} for pure materials and/or alloy systems, provided that the equilibrated solid-liquid interface can be obtained.

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