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METHODS TO DETERMINE SOLID - LIQUID SURFACE ENERGIES I

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SUMMARY

The methods currently available to measure solid-liquid surface energies for organic, inorganic materials, pure metals and alloys are individually examined and discussed.

KATI - SIVI YÜZEY ENERJİLERİNİ BELİRLEME METODLARI

ÖZET

Organik, inorganik maddeler, saf metaller ve alaşımların yüzey enerjilerini ölçmek için kullanılan metodlar ayrı ayrı incelendi ve tartışıldı.

1. INTRODUCTION

The free energy σ_{sL} of a solid-liquid interface is an important factor in nucleation, crystal growth from melt, welding phonomena, liquid phase sintering, Ostwald ripening and embrittlement of solids by liquid metals. These examples emphasise the importance of solid-liquid surface energies in understanding solid-liquid transformations and for having quantitative values of the interfacial energies involved.

Unfortunately it is not easy to measure σ_{SL} even for a pure material and very little progress has been made in its measurement for multicomponent system. Most estimates for σ_{sL} have been made indirectly from homogeneous nucleation studies [1- 6] . These will be discussed and the values obtained compared with the σ_{sL} values obtained from other indirect methods, (crystal growth techniques) and theoretical methods.

The theoretical methods will be briefly outlined and a review of the experimental techniques will be given.

DETERMINATION OF σ_{sL} FROM HOMOGENEOUS NUCLEATION THEORY

Nucleation theory is based on the early work of Volmer [7] , Becker and Döring [8] , Turnbull and Fisher [9] and Turnbull [1] and many others. Until recently almost all experimental values of σ_{sL} were obtained by homogeneous nucleation experiments (involving the supposed homogeneous nucleation of solid from an under-cooled melt) performed originally by Turnbull and co-workers, [1- 6] .

In these experiments the nucleation rate is measured as a function of the maximum undercooling. The nucleation rate is given as

$$I \simeq \frac{kT}{h} n. \exp\left(\frac{-\Delta G_c - \Delta G_A}{kT}\right) \qquad (1)$$

where n is the total number of molecules per unit volume, k and h are Boltzmann's and Planck's constant respectively. ΔG_A is the activation energy of the diffusion process and ΔG_c is the critical excess free energy which is given as

$$\Delta G_c = \frac{16\pi\,\sigma_{sL}}{3\,\Delta S_f^2\,\Delta T^2} \qquad\qquad \Delta T = \frac{2\,\sigma_{sL}}{\sqrt{c}\,\Delta S_f}$$

From the nucleation rate and maximum undercooling measurements, the magnitude of ΔG_c and hence r_c and σ_{sL} can be found. A number of theoretical treatments have provided more refined values for the pre-exponantial term in the above expression for the nucleation rate [10] . The theoretical refinements are mainly concerned with the magnitude of the partition function for the critical nucleus and whether or not rotation and translation of the nucleus should be taken into account. In practice, the temperature dependence of the nucleation rate, I, is found to be very large and hence the exact magnitude of the first term in the above expression is perhaps not too critical.

In order to avoid heterogeneous nucleation by insoluble impurities, the experiment should always be carried out on small droplets (typically a few microns to a few hundred microns in diameter). In such a droplet, the formation of a simple nucleus is sufficient to bring about rapid overall transformation. In early experiments, the particles were generally dispersed as a suspension in some suitable fluid and the nucleation rates were measured by dilatometery [3, 4, 5, 11] . In more recent work direct observation of individual particles has been employed using a hot stage fitted to either an optical microscope or an electron microscope [12, 13] . In the case of direct observation methods, an inert substrate is required to support the particles. This usually consists of freshly blown quartz or pyrex glass which is apparently free of heterogeneous nucleation site.

Table-1 shows a summary of σ_{sL} values obtained from these experiments for a wide range of pure metals and also organic and inorganic substances [14, 15] .

In conclusion ;

a) The values of σ_{sL} derived by this method refer to tempearture significantly below the equilibrium melting temperature (usually around 0.8 T_m). The surface entropy also needs to be known and this is not generally known.

b) σ_{sL} values are averaged over all orientations present in the nucleus.

c) There is still some uncertainty as to whether nucleation is strictly homogeneous under these conditions. The substrate or matrix may have some influence. So measurement of σ_{sL} by homogeneous nucleation experiments are likely not to be accurate and interpretation of data on multicomponent system is likely to be too complex to be of immediate value [16] .

3. THEORETICAL DETERMINATION OF SOLID-LIQUID SURFACE ENERGY

Experimental determination of σ_{sL} is difficult and so attention has been paid to theoretical approaches in evaluating σ_{sL}. These theoretical approaches will be discussed briefly and the estimated σ_{sL} values from these approaches will be compared with the values obtained by the homogeneous nucleation method.

Skapski [17] has attempted a calculation of σ_{sL} based on the nearest neighbour bonding approach. From this approach σ_{sL} was obtained as (valid at the melting point of a pure material).

$$\sigma_{sL} = \frac{mL_f}{\Omega_s} + \frac{2}{3} \frac{\Delta V}{V_s} \sigma_{sL} \tag{2}$$

where m is the fraction of nearest neighbour atoms lying in an adjacent layer. L_f is the latent heat of fusion, $\Delta V/V$ is the relative change of molar volume on melting, Ω_s is the area of one mole of atoms in a solid monolayer.

In order to calculate σ_{sL} from Skapski's theory it has to be assumed that

$$\sigma_{sV} = \sigma_{sL} + \sigma_{LV} \tag{3}$$

This is not strictly true in general, in fact there is experimental evidence that in some system $\sigma_{sV} < \sigma_{sL} + \sigma_{LV}$ where as, in others σ_{sV} may well be greater than $\sigma_{sL} + \sigma_{LV}$. However, the solid-liquid surface energies which are obtained by Skapski's theory are in reasonably good agreement with Turnbull's homogeneous nucleation theoretical results, (Table-1).

Zadumkin [18] has proposed a similar approach to measure σ_{sL} for pure materials which is based on electron-ion core interactions and volume change (so thus density change) on melting. Zadumkin's results also agree reasonably well with Turnbull's result, (Table-1).

Table 1. Estimated solid-liquid surface energies (erg /cm²)

	From Hom. Nucleation		Theoretical Predictions	
Materials	Turnbull [4,5] & others	Zadumkin [18] & others	Waseda & Miller [21]	Kotze & Kuhlmann-Wilsdorf [22]
Mercury (Hg)	23 [6, 12] 24.4 [4,5] 31.2 [3]	25 [18]	21.8	
Water (H_2O)	28.3 [12] 32.1 [4]	16 to 25 [35,37] 20 ± 2 [46]	-	39
Gallium (Ga)	40.4 [12] 56 [5]	41 [18]	52.7	58
Tin (Sn)	54.5 [5] 59 [12] 61.3 [54] 65 [6] 70.6 [69]	49.5 to 61.3 [43] 60 [18]	53.6	44
Bismuth (Bi)	54.4 [5] 79.3 [69] 60.2 [12]		59.2	68
Lead (Pb)	33 [5] 69 [13]	26 [18] 32 [17] 34.6 to 42.7 [43] 55 [20]	50.2	34
Antimony (Sb)	101 [5]		115.5	83
Aluminium (Al)	93 [5]	97 [18] 121 [20]	141.0	113
Germanium (Ge)	181 [5] 251 [12]		202.0	216
Silver (Ag)	126 [5] 143 [12]	85 [18] 101 [17] 136 [20]	156.9	107
Gold (Au)	132 [5]	110 [18] 121 [17] 148 [19]	167.7	127
Copper (Cu)	177 [5] 200 [12]	128 [17] 132 [18]	227.7	141
Manganese (Mn)	206 [5]	-	250.5	244
Nickel (Ni)	255 [5]	-	325.2	270
Cobalt (co)	234 [5]	-	303.6	219
Iron (Fe)	204 [5]	-	264.3	255
Palladium (Pd)	209 [5]	-	252.1	185
Plantinum (Pt)	240 [5]	230 [18] 236 [17]	312.0	261
Sodium (na)	20 [70]	15 [17] 20 [20]	22.0	16
Lithium (Li)	30 [70]	27 [17] 29.7 [20]	36.1	25
Silicon (Si)	-	-	331.5	-

A fundamentally different approach was proposed by Ewing [19, 20] who takes into account both contribution of the melt ($\sigma_{cL} = -\Delta T_E \Delta S_{sL}$) and contribution of the crystal ($\sigma_{cL} = nL_f/4Na$)to σ_{sL}. Therefore

$$\sigma_{sL} = \frac{nL_f}{4N_a} - T_E \Delta S_{sL} \tag{4}$$

where n is the density of atoms in the surface, N_a is Avagodro's number, T_E is the equilibrium temperature and L_f is the latent heat of fusion.

In Ewing's approach it is assumed that the calculations have been performed for an automatically smooth, densely packed crystal-melt interface of a monoatomic substance at the equilibrium temperature. The first term at the RHS of equation (4) was computed using the nearest neighbour interaction approximation and the second term was calculated from known values of the radial distribution of the bulk liquid, g(r), of the material. Ewing's approach was used by Waseda and Miller [21] to estimate σ_{sL} values for a large number of metals leading to reasonably good agreement with Turnbull's data, (Table-1).

An empirical relation was proposed by Kotzé and Kuhmann-Wilsdorf [22] who calculated the energies of high angle grain boundaries and in order to evaluate σ_{sL}, assumed σ_{sL} to be half of the grain boundary energy σ_{gb} at the melting temperature. A similar kind of method (assuming σ_{sL}/σ_{gb} = 0.45 and that the grain boundary structure and σ_{sL} remain constant throughout the alloy range) was used to calculate σ_{sL} for metals by Miller and Chadwick [23]. σ_{sL} was calculated by studying the change in σ_{sL}/σ_{gb} for an alloy system as a function of alloy composition and extrapolating the results for the pure material which was one of the components of the alloy.

Some attempts have also been made to evaluate σ_{sL} for binary alloys by Eustathopoulos and co-workers [24- 29] and Warren [30] on the basis of thermodynamic considerations.

Eustathopoulos and co-workers have used a monolayer nearest neighbour interaction model for an automatically rough interface in a binary A - B system with A as the major component of the solid solution. The equilibrium roughening transition of solid A in contact with molten component B has been studied by analysing the shape of a small liquid B droplet inside a solid A matrix. For the equilibrium condition, an expression is obtained for σ_{sL} and from this expression σ_{sL} is evaluated for binary alloys, (Table-2).

Warren [30] also proposed a similar method calculating σ_{sL} in binary systems which is based on the molar free energies of solid component A, liquid component B and the disturbance of the solid-liquid interface at equilibrium. It was assumed that at equilibrium the molar free energies of the phases will be functions of composition (at an interface of two atomic layers) because some liquid B atoms diffuse in to the solid A matrix and some solid A atoms diffuse in to the liquid B matrix. This causes a finite increase in the interfacial energy because of the disturbance at the interface. From this disturbance effect on chemical composition (thus molar energy) and the structural disturbance on σ_{sL} has been calculated for binary alloys, (Table-2).

Miedema and den Broeder [31] and Nason and Tiller [32] have used similar kinds of methods to measure σ_{sL} for pure materials and binary alloys, assuming one of the components A is solid and other component B is liquid. In fact, as can be seen from any binary equilibrium phase diagram neither solid phase nor liquid phase is a function of the single component, both phases (at least liquid phases) are always functions of both components, so for more reliable σ_{sL} calculation the effet of the components on the phases (i.e. properties of the new alloy phases) must be taken into account.

4. DETERMINATION OF σ_{sL} FROM CRYSTAL GROWTH

Solid - liquid surface energy has a great influence on numerous aspects of crystal growth such as the morphological stability of a planar interface [33 - 37] , dentritic growth [38 - 41] and eutectic growth [42 - 44] .

If a solid-liquid interface grows very slowly from its melt, the interface will often be flat or planar. However, if the growth rate increases a smooth interface becomes unstable and small protrusions form at the solid-liquid interface. The formation of these protrusions is partly governed by σ_{sL} since, their existance results in a higher interfacial area and consequently an increase in the energy of the system. σ_{sL} can be calculated by interpreting the information from these interface protrusions and using Mullings and Sekerka's morphological stability theory, [45] .

This principle has been used to calculate σ_{sL} for the ice-water system by Hardy and Coriell [34 36] and Hardy et at [37] . σ_{sL} values (16 to 25 erg/cm^2) derived by this technique were almost half that of the values obtained by direct methods, [71] One conclusion is that the calculation of σ_{sL}, using the stability theory and obtaining the necessary information by direct observation of the slowly growing interfacial protrusions is difficult to apply to trasparent materials and even more difficult for opaque systems.

Kotler and Tarshis [46] have used a dendritic growth method based on Temkin's analysis (which takes account of the velocity and curvature of the dendrite tip by assuming that the tip region can be described as a paraboloid) to calculate σ_{sL} for ice-water. They found σ_{sL} (20 ∓ 2 erg/cm^2) to be approximately 30 % less than the homogeneous nucleation results and 50 % less than the values obtained directly under near equilibrium condition. Application of the same method by Kotler and Tarshis [47] and a similar method by Trivedi [38] for white phosphorus have given even lower values of σ_{sL}, [71] As Trivedi [38] and Jones [16] pointed out use of the dendritic growth method to measure σ_{sL} is unlikely to be accurate because of the close proximity of neighbouring dendrites.

Jordan and Hunt [43] have estimated σ_{sL} for Sn and Pb using the Jackson Hunt theory [42] and measured lamellar and rod spacings, ($\lambda^2 V$ = constant) and lamellar-rod undercooling ΔT, ($\Delta T/V$ = constant, V is the growth velocity). Their results for Sn and Pb are in reasonable agreement with Turnbull's homogeneous nucleation results, (Table-1). However, application of the method for the Al - $CuAl_2$ system was not successful

Table: 2. Estimated solid-liquid surface energy for selected binary alloys (erg/cm²)

Alloy Solid - liquid	Surface energy erg/cm^2
Al - Al	93 [5] to 141 [21]
Al - Sn	157 ± 18 [28], 227 [30] 345 ± 15 [72, 73]
Al - In	238 ± 10 [72]
Cu - Cu	128 [17] to 227.7 [21]
Cu - Pb	232 ± 25 [28], 339 [30], 310 ± 10 [72]
Zn - Zn	87 [74]
Zn - Sn	99 ± 10 [28], 119 [74]
Zn - In	122 [74]
Zn - Bi	148 [74]
Zn - Pb	185 [74]
Fe - Fe	254 [29]
Fe - Co	430 [29], 443 [30]
Fe - Pb	1080 [29]
Fe - Ag	1370 [29]
Co - Cu	405 [30]
W - Cu	1130 [30]
W - Ni	715 [30]
C - Cu	3930 [30]
C - Ni	2120 [30]

and this method has not been used as an estimate for other systems up to date.

In conclusion, estimations of the solid-liquid surface energy, σ_{sL} by theoretical and indirect experimental approaches is not easy and it is even more difficult to measure σ_{sL} by direct experimental approaches. These experimental techniques will be reviewed briefly and σ_{sL} values derived from them will be discussed.

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

Any theoretically calculated σ_{sL} values need to be supported by experimentally obtained σ_{sL} values otherwise the theoretical values cannot be relied on. Therefore, attention has been paid to experimental techniques designed to produce σ_{sL} measurements. The experimental σ_{sL} measurements for pure and multi-component systems can be determined using one of the following methods :

1) From the measurement of dihedral angle.
2) From direct application of the Gibbs-Thomson equation, [71] .

5.1. DETERMINATION OF σ_{sL} FROM THE MEASUREMENT OF DIHEDRAL ANGLE

5.1.1. Equilibrium at Three Phase Junction

When three phases are at equilibrium the condition of equilibrium at the junction of the phases 1, 2 and 3, (Fig.1) is given by the relation [48] .

$$\frac{\sigma_{12}}{\text{Sin} c} = \frac{\sigma_{23}}{\text{Sin } a} = \frac{\sigma_{31}}{\text{Sin} b} \qquad (5)$$

Thus a knowledge of the angles of intersection of the interfaces (which may be measured directly) gives the relative values of the surface energies (isotropic) associated with the interfaces. Note that equation (5) is strictly true only if all the phases are fluid, (i.e : it is not directly applicable to solid-melt interface) because of the anisotropy of the σ_{sL}. For an isotropic σ_{sL} the equilibrium conditions at the triple junction must be corrected in order to take into account Herring's torque term [49] . One application of the three phase equilibrium method is the "sessile drop" technique which uses the equilibrium of a liquid on a solid surface (Fig.2). In this case equilibrium will only be achieved when the solid and liquid are also in equilibrium with the surrounding vapour (which is not easy to achieve). Assuming that the equilibrium at the three junction (for isotropic σ_{sL}) is achieved, (Fig.2), then this state may be represented by the equations :

$$\sigma_{gb} = 2 \ \sigma_{sv} \operatorname{Cos} \left(\frac{\theta_{sv}}{2}\right) \quad \text{(for solid vapour equilibrium, fig.2a)} \tag{6a}$$

$$\sigma_{sv} = \sigma_{sL} + \sigma_{Lv} \operatorname{Cos} (\theta_{Lv}) \quad \text{(for vapour-liquid-solid equilibrium, fig. 2b)} \tag{6b}$$

$$\sigma_{gb} = 2 \ \sigma_{sL} \operatorname{Cos} \left(\frac{\theta_{sL}}{2}\right) \quad \text{(for solid-liquid equilibrium, fig. 2.2c)} \tag{6c}$$

where σ_{gb}, σ_{sv}, σ_{Lv} and σ_{sL} are the grain boundary, solid-vapour, liquid-vapour and solid-liquid surface energies respectively and θ_{sv}, θ_{lv} and θ_{sL} are as described in fig.2.

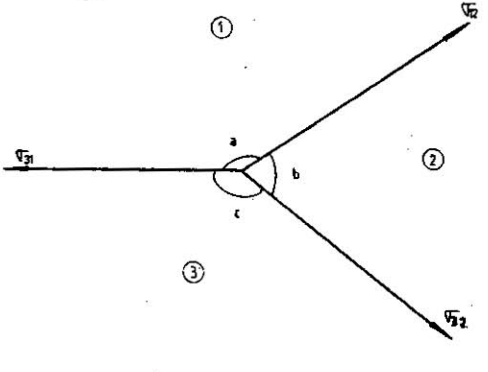

Fig.1. Equilibrium intersection of tree interfaces

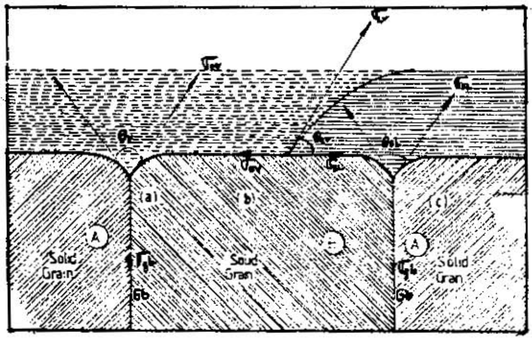

Fig.2. Mulitiphase equilbrium in a solid-liquid-vapour system.(After ref.29)

σ_{sL} can be found for any suitable pure material from equation (6), considering only high-angle grain boundaries and provided that σ_{sv}, σ_{sL} and σ_{Lv} are measured and σ_{Lv} and σ_{gb} are known. This principle has been used by Ketcham and Hobbs [50] to measure σ_{sL} for the ice-water system. The values of σ_{sL} (33 ± 3 erg/cm^2) for ice-water obtained by Ketcham and Hobbs is smaller than the previously measured σ_{sL} for ice-water by other direct methods, [71]. Suzuki and Kuroiwa [51] found that Ketcham and Hobbs had failed to measure σ_{sv} correctly and thus σ_{sL} for ice-water and an appropriate correction gives a value of σ_{sL} for ice-water which is in good agreement with other direct measurements. Ketcham and Hobbs' contact angle measurement has also been questioned by Knight [52]. The technique has not been applied to any other pure material up to date but has been used for dissimilar phases such as solid copper-liquid lead and solid aluminium-liquid tin but the validity of the method is questionable. When measuring σ_{sv} both the grain boundary and solid surface are pure however, when measuring σ_{sL} the grain boundary is often highly contaminated by the liquid phase and σ_{gb} cannot always be eliminated from equations (6) as required. Also for this kind of experiment (i.e. sessile drop experiments) σ_{Lv} is not obvious and σ_{sv} is not necessarily constant because of contamination of the solid phase from the liquid droplet. As discussed by Singiorgi et al [53] the accuracy of σ_{sL} by the sessile drop method is also dependent on the droplet profile geometrical anisotropy of the interfaces. Therefore, due to these disadvantages, σ_{sL} measurement by the "sessile drop" for pure materials is questionable and the method is not applicable for multicomponent systems.

5.1.2. Determination of σ_{sL} Relative to σ_{gb} by Measurement of Dihedral Angle

An attempt to estimate σ_{sL} relative to the grain boundary energises, σ_{gb} by measuring the dihedral angle at the grain boundary root, (fig.3) has also been made by Glicksman and Vold [54 - 55] for bismuth. The solid-liquid equilibrium shape was observed directly by using transmission electron microscopy of a thin film of the metal. The specimen was in the form of a thin (approximately 2000^{o}A) vapour deposited film of bismuth sandwiched between thin carbon films, mounted on the hot stage of an electron microscope. A radial temperature gradient with the highest temperature at the centre was imposed on the specimen. The equilibrium shape, (Fig.3) may be represented by Herring's torque terms, [49] ;

$$\sigma_{gb} - 2\,\sigma_{sL}\,\mathrm{Cos}\,\varphi - 2\,\frac{\partial\,\sigma_{sL}}{\partial\,\varphi}\,\mathrm{Sin}\,\varphi = 0 \qquad \text{(Herring's equation)} \qquad (7)$$

where φ is the dihedral angle, σ_{gb}, σ_{sL} are as described before and $\partial\sigma_{sL}/\partial\varphi$ expresses any dependence of σ_{sL} on the crystallographic orientation exposed to the liquid phase. Evaluation of σ_{sL} was made by measuring the dihedral angle of the groove in the solid-liquid interface, 2φ and the angle of tilt of the solid-solid boundary, θ , (Fig.3). The values of σ_{sL}, (61,3 erg/cm^2) for bismuth was decuded by neglecting the the torque term $\partial\,\sigma_{sL/\partial\varphi}$ and by calculating σ_{gb} from the known free energy of edge dislocations in the solid.

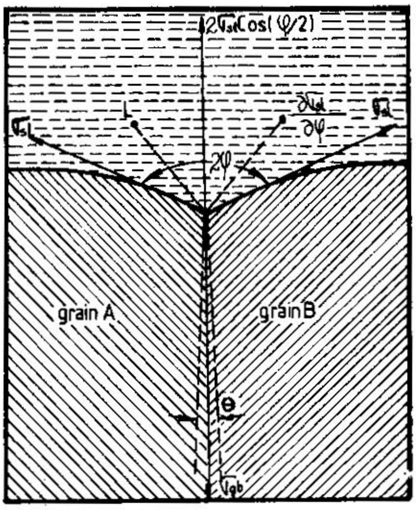

Fig.3. Intersection of a symmetric tilt boundary with the solid-liquid interface (After ref. 54)

Application of this method is quite difficult because many materials rapidly evaporate or globulate at elevated temperatures, especially under the condition of high vacuum prevailing in the electron microscope. This method cannot be applied to alloys because alloys usually do not have low angle tilt boundaries (probably due to segregation effects at the grain boundary) and it is difficult to calculate σ_{gb} with sufficient accuracy.

5.2. DETERMINATION OF σ_{SL} FROM DIRECT APPLICATION OF THE GIBBS-THOMSON EQUATION

The most effective methods for measuring solid-liquid surface energy, σ_{SL}, experimentally involve the direct application of Gibbs-Thomson equation. This equation is formed by combining the condition of mechanical equilibrium of a curved interface and the condition of chemical equilibrium. If all other intensive variables (such as composition, pressure and strain energy) remain constant, a solid bounded by an interfacial element having principle radii of curvature r_1 and r_2 measured in the solid will be in equilibrium with its melt at a temperature T_r (which is not equal to the phase diagram liquids T_m) the Gibbs-Thomson equation for this is given by,

$$T_m - T_r = \Delta \Gamma_r = \frac{\sigma_{SL} V_{si}}{\Delta S} \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (8)$$

where V_{si} is the partial volume of the solid i^{th} component, ΔS is the entropy of fusion, (in the case of an alloy system weighted entropy fusion, ΔS^* is used instead of ΔS).

The solid-liquid surface energy, σ_{SL} can be evaluated directly from the Gibbs-Thomson equation provided that ΔT_r is measured for known values of r_1 and r_2 for a system at equilibrium and ΔS is known independently.

However, in practice there are several difficulties associated with using the Gibbs-Thomson equation. If a single crystal of solid is surrounded by its melt at the equilibrium temperature, its condition of equilibrium is very unstable, for a small temperature fluctuation causes either total melting or total solidification. Therefore, a constant temperature is needed to achieve a stable equilibrium condition.

Various techniques have been suggested to measure σ_{SL} directly from the Gibbs-Thomson equation. These techniques will be discussed individually.

5.2.1. Skapksi's Method

This was the first successful attempt to measure σ_{sL} by the direct application of the Gibbs-Thomson equation using transparent materials (myristic, luric, stearic acids, ice-water and benzene) and wedge shaped geometry to observe the capillarity effect and therefore to measure ΔT_r, r_1 and r_2, [56 - 58] .

The wedge shape apparatus (Fig.4a) gives a temperature which is stable with respect to small fluctuations in temperature. If for example the temperature decreases, the solid will grow so as to increase the curvature of the solid-liquid interface to restore the equilibrium as described by equation (8). A similar argument applies to small increases in temperature. So for accuracy the temperature must be as stable as possible with a zero temperature gradient in the system.

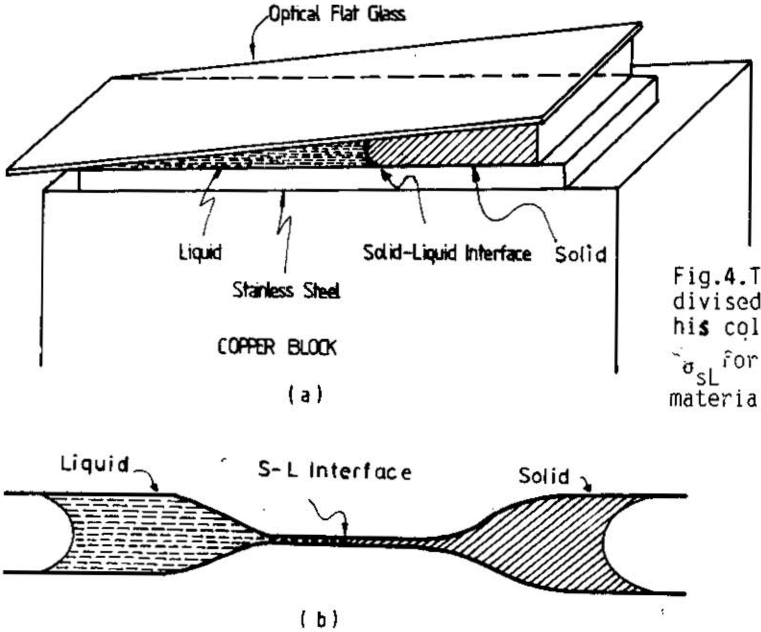

Fig.4.The arrangements divised by Skapski and his colleagues to measure σ_{sL} for pure transparent materials

The presence of the liquid-vapour meniscus the solid-liquid system to be at a pressure of less than one atmosphere, this leads to a related change in T_m. In order to eliminate meniscus effects, Skapski et al [57] refined their apparatus employing a tempering capillary cylinder which also allows r_1 and r_2 to be measured directly (Fig.4b).

Reasonable σ_{sL} values can be obtained for very pure transparent materials with Skapski's method. However this method cannot be used for impure or alloy systems. If the material is not pure enough, impurities might segregate into the thinner part of the wedge or the tapered cylinder (i.e. in the liquid) thereby causing lower melting points there which cause an error in ΔT_r and thus in σ_{sL}.

5.2.2. The Melting Points of Small Crystals

If a small isolated crystal is heated its melting point shows some depression which is dependent on its size. Melting begins at the solid-vapour interface and the solid is surrounded by a very thin liquid skin. At first the liquid skin will be too thin for the liquid to be thought of as having the bulk phase properties but when the liquid has a certain thickness (critical thickness) equilibrium will be achieved provided the solid is still large enough to have its bulk phase properties. At the equilibrium condition for the solid-liquid interface of a small crystal the Gibbs-Thomson equation (for isotropic σ_{sL}) may be derived as [59]

$$T_m - T_r = \Delta T_r = \frac{2T_m}{L}\left[\frac{\sigma_{sL}}{\rho_S(r-t)} + \frac{\sigma_{sL}}{r}\left(\frac{1}{\rho_S} - \frac{1}{\rho_L}\right)\right] \qquad (9)$$

where r is the initial radius of the crystal, t is the critical thickness of the liquid, ρ_S and ρ_L are the densities of the solid and liquid phases respectively and T_m, T_r, L, σ_{sL} and σ_{sv} are as described before.

The surface energies for different materials have been obtained via the depression of melting point technique by Combes, [60 61], Wranski [59] and Samples [65] using selected area diffraction in vacuum a electron microscope. Especially this group has tried to improve the depression of the melting point of small crystal technique and applied it to small thin, [59], lead [61], bismuth [60] and gold [65] crystals (usually 10 nm to 100 nm). Their results showed that equation (9) was appropriate to these metals all but bismuth. Using this technique the major source of uncertainty arises with the assumption that the melting occurs by uniform surface melting.

A related method for measuring σ_{sL} has been attempted by Kubelka and Prokscha [62] where they measured the depression of melting point of ice, solid benzene and ethylene dibromide absorbed in porous media such as silica gel. A similar experiment was carried out by Puri and his colleagues [63 - 64] later on, using the values from their data [62 - 64] , σ_{SL} was recalculated and analysed by Jones [16] but the technique was found to be unreliable for the following reassons :

a) σ_{SL} values for a given material show inconsitency from one experiment to another.

b) r values may be in error, since a capillary closed at one end alters the vapour pressure considerably.

c) The effect of surface forces from the container on a material (observed in a capillary) is probably very large.

5.2.3. Liquid Inclusion Stationary in a Temperature Gradient

Above the solidus temperature an impure solid, usually contains a large number of liquid droplets. These droplets migrate up the tempearture gradient [66 - 68] because of dissolution at the hotter part of the solid-liquid interface and solidification at the colder part of the interface (Fig.5). This proccess continues until the system reaches equilibrium. However sometimes droplets are immobilised because of the interaction between the droplet and a grain boundary in a direction

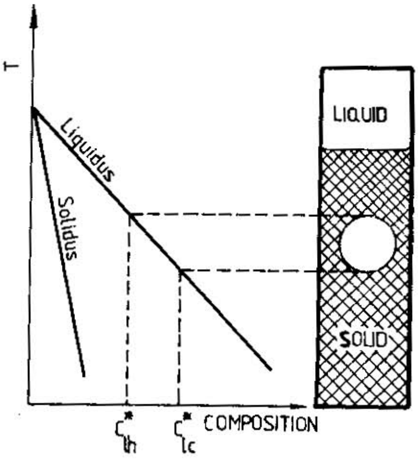

Fig.5.Mechanism of TGZM (from ref.68)

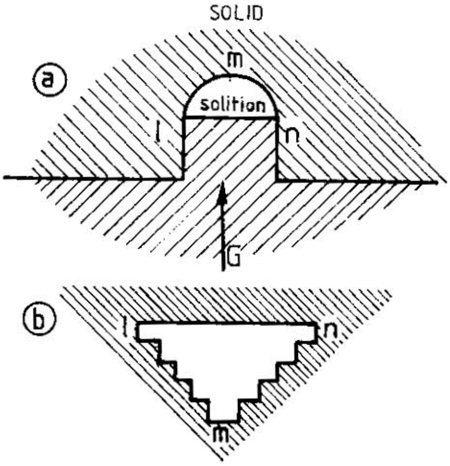

Fig.6.Schematic illustration of impure liquid droplets immobilized in a solid subjected to G.(from ref. 16)

perpendicular to the temperature gradient (Fig.6) or crystal effects (such as screw dislocations).

The solid-liquid interfaces reach equilibrium when they have not been affected by the immobilisation processes. At equilibrium the stationary droplets must be quite uniform and therefore the shape will be described by the Gibbs-Thomson equation and from this equation σ_{sL} can be calculated. Clearly analysis of the droplet shapes will be more convinient and simple for the system having equal solid and liquid thermal conductivities ($K_S = K_L$) allowing the thermal distribution at the interface to be readily calculated.

There has been no direct application of this method (which is applicable only for impure systems)to measure σ_{SL} up to date, not only because of the lack of geometrical symmetry and difficulties of the mathematical discription of the droplet shapes but also because the equilibrium is questionable.

6 CONCLUSION

In summary, the teoretical and experimental work of the last forty years to have established a sound body of information on solid-liquid surface energies. However all the methods which are discussed in this paper have difficulties to determine solid-liquid surface energies for microscopic systems. Robably the most attractive method of measuring σ_{SL} directly for microscopic system involves observing the equilibrium shape of grain boundary grooves. The grain boundary groove method will be discussed in another paper[71] .

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