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# Review of Techniques for Thermophysical Property Measurements at High Temperatures

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**Abstract**

The methods available for the measurements of the following thermophysical properties of high temperature melts are reviewed viz. density, viscosity, surface tension, heat capacity, enthalpy, thermal diffusivity and conductivity, electrical conductivity and emissivity. The methods are illustrated with reference to work carried out on molten silicon. In order to combat contamination of the melt from container/sample reactions there has been a gradual switch to the use of (i) containerless methods employing various forms of levitation or microgravity (drop towers, parabolic flights and space experiments) and (ii) sub-second rapid heating and other non-intrusive techniques. However, there are other equally-important conditions which must be addressed to obtain accurate property values, e.g. the control of oxygen partial pressure in surface tension measurements and the selection of the most reliable method to analyse data. It is our contention that equal attention should be given to these problems.

Keywords: physical properties; techniques; high temperatures; silicon.

## 1. Introduction

Mathematical modelling has proved an exceedingly useful tool in improving both process control and product quality. There are a variety of models available which seek to describe the thermodynamics, kinetics, heat transfer and fluid flow in a process. Our major involvement has been with the models describing the heat and fluid flow of processes and these models have proved reasonably successful in a wide spectrum of applications, secondary refining, welding, casting and solidification etc. Furthermore, as these models have improved they have developed to the stage where one of the prime requirements is for accurate thermophysical property data for the materials involved.

However, many of the processes involve materials which melt at high temperatures and these temperatures make measurement difficult. The unofficial First Law of High Temperatures states "*At high temperature everything reacts with everything else*" and the Second Law that "*They react quickly and the situation gets progressively worse as the temperature increases*".

Thus the reactivity of the melt becomes a major problem since it attacks virtually all containers to some extent and thereby the melt is contaminated and may eventually escape from the container causing damage to the apparatus. Consequently, many ingenious techniques have been developed to combat the problems of reactivity of the melt. Many of these novel techniques have been used in studies of the thermophysical properties of silicon. Consequently, in this review of the techniques for the measurement of the thermophysical properties of high temperature melts, in most cases specific reference will be made to the measurements carried out on silicon. In the second part of this investigation, the values of thermophysical properties reported for silicon have been collated and evaluated.

The interest in thermophysical properties of silicon stems from the need for these data to improve the modelling predictions. These are needed to help overcome the problems encountered when increasing the size of silicon single crystals from their current 8" to 12"[1,2]. Consequently, data are required for the properties associated with fluid flow (density {$\rho$}, viscosity {$\eta$}, and surface tension {$\gamma$} and their temperature dependencies) and heat transfer (heat capacity {$C_p$}, enthalpy {$\Delta H$}, thermal diffusivity {$a$} and conductivity {$\lambda$} and emissivity {$\varepsilon$} as functions of temperature). Many of the techniques used to measure the thermophysical properties have focused on the reactivity of silicon (particularly with the containers and with the partial pressure oxygen above the melt) and this has led to the use of containerless methods and non-intrusive techniques.

**2. Containerless and Non-Intrusive Techniques**

Containerless techniques eliminate reaction between the container and the molten sample and thereby avoid contamination of the melt.

Non-intrusive techniques can either (i) use a crucible but do not involve the insertion of probes into the melt and tend to involve monitoring light, laser or thermal rays or observations of the sample, or (ii) involve such rapid heating that measurements can be obtained for the liquid phase before the specimen collapses.

Containerless measurements can be divided into two types which involve (i) levitation (using electromagnetic, aerodynamic, acoustic or electrostatic forces), (ii) micro-gravity (using drop towers, *sub-orbital* flights and space flights).

2.1. Non-Intrusive Techniques

These techniques used for measurements on liquid can be classified into two types:

(i) Methods where measurements are made when a thermal, light or laser beams are directed onto the surface of the melt or visual observations are made, typical examples are:
- pendant drop, drop weight methods for surface tension[3]
- laser pulse (or flash) methods for thermal diffusivity
- surface laser light scattering method[4].

(ii) Rapid heating methods where the specimen is heated so rapidly that some measurements can be obtained for the liquid phase (because of surface tension forces) before the sample collapses, typical examples are:
- subsecond (pulse) or explosive wire technique used for measurements of $C_p$, enthalpy, $\rho$, electrical conductivity, $\varepsilon$ and $\gamma$[5,6,7].

In the plane temperature wave method a modulated electron beam is focused onto the surface of a disc-shaped specimen and the thermal diffusivity is determined by monitoring both the phase lag and the temperature transient at the back face[8]. The measurements can be obtained at either a constant temperature or dynamically at heating rates of up to 100 $Ks^{-1}$. Only the central portion of the specimen is allowed to heat when carrying out measurements for the liquid.

2.2 Levitation Methods

The following methods have all been used in physical property measurements:

*Electromagnetic levitation (EML)*

Levitation is achieved by coupling a special coil to a RF power source. The repulsive force required for levitation is provided by the reaction of the eddy currents (induced in the surface of the sample) to the primary field produced by the lower windings of the coil. The upper counterwindings create a null point in the magnetic field which permits stable positioning of the sample. 'Cold crucibles' (CCL) provide an alternative form of electromagnetic levitation in which levitation results from the repulsion of like charges on the sample and crucible. Both forms of electromagnetic levitation are restricted to materials with high electrical conductivity, e.g. metals and some carbides and sulphides.

*Acoustic levitation (ACL)*

High intensity sound waves are used to generate sufficient force to counteract the gravitational forces[9]. A reflector is used to produce a minimum acoustic pressure zone and thus provide stable positioning of the sample. This form of levitation can be applied to both conducting and non-conducting materials but cannot be used in vacuum.

*Aerodynamic (gas jet) levitation (ADL)*

High velocity gas flow from specially-designed nozzles are used to levitate the sample. The spreading action of the jet can be used to position the sample which can be further improved by electromagnetic stabilisation. Liquids tend to fragment in the gas flow but recently, investigations on molten metals have been successfully carried out[10,11].

*Electrostatic levitation (ESL)*

The charge-carrying sample is levitated in an electrostatic field generated between two or more electrodes. Since there is no potential minimum for an electrostatic field, stable positioning of the specimen can only be obtained with a feedback mechanism[12].

Levitation techniques provide the follow advantages:

a) they eliminate contamination of the melt through sample-container reactions
b) they permit large undercoolings.

However, they do have the following disadvantages:

(i) Temperatures can only be measured by pyrometric techniques and are prone to more uncertainty since reliable emissivity values are needed.
(ii) There may be large temperature gradients in the sample when heating is by laser beams (e.g. acoustic and aerodynamic levitation) and the use of 3 lasers are recommended to minimise these gradients.
(iii) Corrections may be needed to account for the effects of electromagnetic or electrostatic forces

(e.g. on the surface tension values obtained by the oscillating drop method[13,14]).

(iv) Experiments can not be carried out in vacuum in acoustic and aerodynamic levitation (e.g. measurements of ($C_p$/emissivity) from cooling curves).

2.3 Microgravity Methods

Thermophysical property determinations have been carried out using drop tubes, sub-orbital (parabolic and sounding rocket) flights and space flight experiments. Microgravity conditions only apply for about 10s in drop tube and parabolic flights and thus measurements must be made quickly. Microgravity experiments are very expensive and consequently should only be applied when measurements can not be obtained in terrestrial experiments. Consequently, they should be primarily used to provide reference values and establish the magnitude of errors arising from convection forces in terrestrial measurements. In addition to the advantages already listed for levitation techniques microgravity experiments have the following additional advantages:

c) Buoyancy driven convection is negligible (thermo-capillary (Marangoni) forces can still occur).
d) They are free from large electromagnetic and electrostatic forces needed to levitate in terrestrial experiments.
e) Certain experiments can only be carried out in microgravity conditions (e.g. oscillating drop[5] used to measure viscosity since electromagnetic forces affect damping).

2.4 Disadvantages of Non-Intrusive Methods

Subsecond, rapid heating methods do produce values which are in reasonable agreement with values obtained using conventional techniques. However, they do have the following disadvantages:

(i) the heating rate is so rapid that property changes resulting from phase transitions are not observed but tend to be smeared out.
(ii) the experimental uncertainties tend to be large.

The advantages and disadvantages associated with various containerless systems and subsecond methods are summarised in Table1 and references for typical measurements on Si are given and other materials where no reported measurements on Si have been reported.

## 3. Other Factors Affecting the Accuracy of Measurement

Recent developments in techniques have tended to focus on the reactivity of the melt at high temperatures and eliminating contamination from sample-container reactions. However, there are other problems which must be addressed and which can be even more important than the contamination problem. These include:

(i) The effect of oxygen (and nitrogen) on the property measurement (this is an especial problem for surface tension measurements).
(ii) The effect of oxide skins (or films) formed on the surface of some metals (e.g. Al, Ti, nickel-based superalloys) and which can interfere with measurements and even alter the property values (e.g. emissivity) or introduce an interfacial thermal resistance during thermal conductivity measurements.
(iii) The effect of convective flows, this is an especial problem in the measurement of thermal conductivities and diffusion coefficients for liquids with low viscosities.
(iv) The non-wetting of the liquid on the container or the probe can lead to low viscosity values and to an interfacial thermal resistance.

**Table 1:** Advantages (a to e) and Disadvantages ((i) to (vii) of containerless processes, as referred to in the text and reference of application to Si and other symbols denoted by footnotes A to H)

| | Advantages | Disadvantages | Measurement | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\rho$ | $\eta$ | $\gamma$ | $C_p$ | a, $\lambda$ | $\varepsilon$ | $\sigma$ |
| Space flights | a, b, c, d, e | (i) | | 15) A | 16) B | 17) C | - | 17) C | 18) |
| Drop tower | a, b, c, d, e | (i) | | - | 3) | - | 3) D | | |
| Sub-orbital flights | a, b, c, d, e | (i) | | - | 2) | | 3) D | | |
| EML - | a, b - | (i) (iii) | 19) | | 20) | 21) D | - | 26) | |
| - CCL | a, - | (i) | | | | | | 22) | |
| ESL | a, b, - | (i) (iii) | 14) | - | 14) | 14) | - | 14) | |
| ADL | a, b, - | (i) (ii) (iii) (iv) | 23) E | | 23) E | | | | |
| ACL | a, b, | (i) (ii) (iii) (iv) | 24) F | | | 25) F | | 2) F | |
| Subsecond | a, b, - | (i) (ii) (v) (vi) | 7) H | | 6) F | 27) H | 8) H | 7,27) H | 7,27) H |

A = amorphous alloy, B = Au, C = Nb, D = InSb, D = Refractory metals, E = Oxides, F = $Al_2O_3(\ell)$, G = Cu, H = various metals.

(v) The analytical method used to derive the property from the measured data, important examples are:
- Three techniques are used to derive viscosities for damping measurements, Iida and Guthrie[28] showed the choice of method can have a significant effect (20%) on the viscosity value (see 29)).
- the use of the time for half maximum temperature rise ($t_{0.5}$) to determine the thermal diffusivity from laser pulse experiments.
- the use of the Cumming's equation in oscillating drop experiments to account for the effect of electromagnetic forces[13] and recently Rhim[14] has presented a correction technique for electrostatic forces.

(vi) Inaccuracies in other physical property data needed in the calculation of property measurements. Typical examples are in the calculation of:
- thermal conductivity from thermal diffusivity requires values for $C_p$ and density.
- crucible radius and moment of inertia requires a knowledge of the thermal expansion coefficient of the container material in oscillating viscometry.

(vii) Inaccuracies in temperature measurement, especially where temperature measurements are the parameter being monitored to provide the property value.

These various factors affect some specific techniques and not others and so they will be dealt with individually in the following text.

## 4. Properties Related to Fluid Flow

### 4.1 Density (ρ) measurements

Contamination of the melt would not be expected to have a marked effect on density measurements unless the contamination was extensive. Consequently, the Archimedean technique would be expected to be reliable providing 1) the effect of surface tension forces are taken care of[29] and 2) for the sessile drop method, computer-software allows more accurate evaluation of density. Thus these conventional techniques should provide density values with an uncertainty of $< \pm 2\%$. A considerable amount of recent work has been focused on the levitated drop method using all forms of levitation. The natural oscillation of the drop results in some difficulty since it is necessary to determine the volume of an asymmetric drop. The drops are usually quite small (4-7 mm diam) and one source of uncertainty is the determination of the edge resolution of the drop and 'flaring' can be a problem in this context. In our experience the best edge resolution can be obtained with optical cameras but we have resorted to a digital camera with slightly inferior resolution because the data can be processed much more rapidly[30]. Experimental uncertainties associated with the levitated drop are probably $\pm 3\%$ although Rhim et al[14] reported uncertainties of $\pm 1\%$ even when using very small (1-2 mm) drops of molten Si. The formation of surface oxide films (e.g. molten Al) can make methods such as the Archimedean and Maximum Bubble Pressure methods very difficult to carry out.

### 4.2 Viscosity (η) Measurements

The oscillating viscometer remains the principal method for measuring the viscosity of liquid metals at high temperatures. The main problems with the technique are:

(i) the analytical method used to analyse data; Iida and Guthrie[28] recommended the Roscoe equation to account for end effects in preference to the Shvidkovskii and Knappwost methods; however the Shvidkovskii was recently used by Kimura et al[1].

(ii) using container materials which are non-wetting to the melt, as can be seen from Figure 1 the viscosity measured using a BN (non-wetting) crucible is significantly lower than the value obtained with a 'wetting' SiC-coated crucible. (It is paradoxical that 'wetting' conditions in high temperature systems usually refer to those where there is some reactivity between sample and container.)

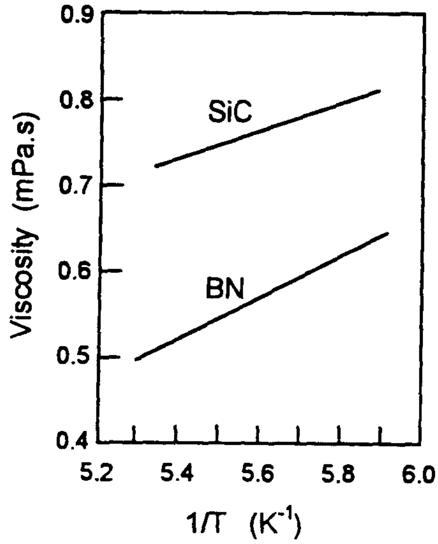


Figure 1 Viscosity of Si as measured in wetting SiC and non-wetting BN crucibles[1].

(iii) Corrections to the measured viscosity to account for thermal expansion of the crucible tend to be quite high at ca. 10% and the density of the sample is needed to calculate the viscosity.

In order to minimise the end effects, recent investigations have tended to use crucibles with large aspect ratios (i.e. height/diameter).

Two novel techniques have been used to measure viscosities. Egry et al[15] measured the viscosities of a molten amorphous-metal alloy measuring the damping of an oscillating drop in microgravity (Figure 2). These conditions are required since electromagnetic forces would swamp the viscous forces present in electromagnetic levitation studies. The results obtained were in very good agreement with measurements obtained by the rotating cylinder method. It will be interesting to see whether it can be applied to pure metals which have lower viscosities.

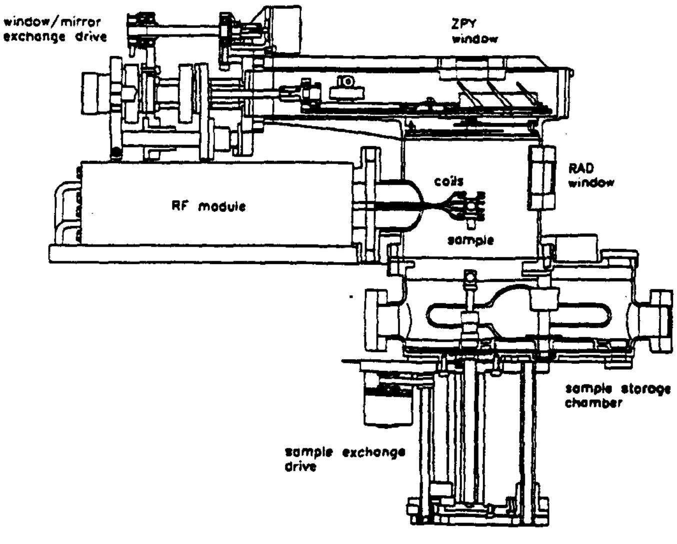


Figure 2 Schematic diagram of the oscillating drop apparatus used to measure viscosities of molten amorphous metals in microgravity.

The other novel technique is the surface laser light scattering (SLLS) method[32] which is described in Section 4.3. Viscosities can be obtained, in theory, from the damping of ripplons, however, the uncertainties in the results increases with increasing diameter of the signal beam and the results were considered to be of insufficient accuracy for publication.

### 4.3 Surface Tension (γ)

The surface tension (γ) and its temperature coefficient (dγ/dT) are particularly important since thermocapillary convention plays an important part in the fluid flow in both Czochralski and Floating Zone methods. Containerless methods for measuring the surface tension since very low (say 50 ppm) levels of surface-active impurities such as O or S can have significant effect on both γ and (dγ/dT). Since liquid metals are frequently contained in oxide refractory crucibles or plaques, contamination of the melt with soluble O (resulting from the reactivity of the metal and crucible) can have a significant effect on both γ and (dγ/dT). It is necessary to differentiate between *soluble* oxygen (denoted O̲) and *combined* O present as oxides, the latter has little effect on surface tension, the reduction in surface tension results from increases in soluble oxygen. Total oxygen analyses are therefore of limited benefit since they contain contributions from oxide particles.

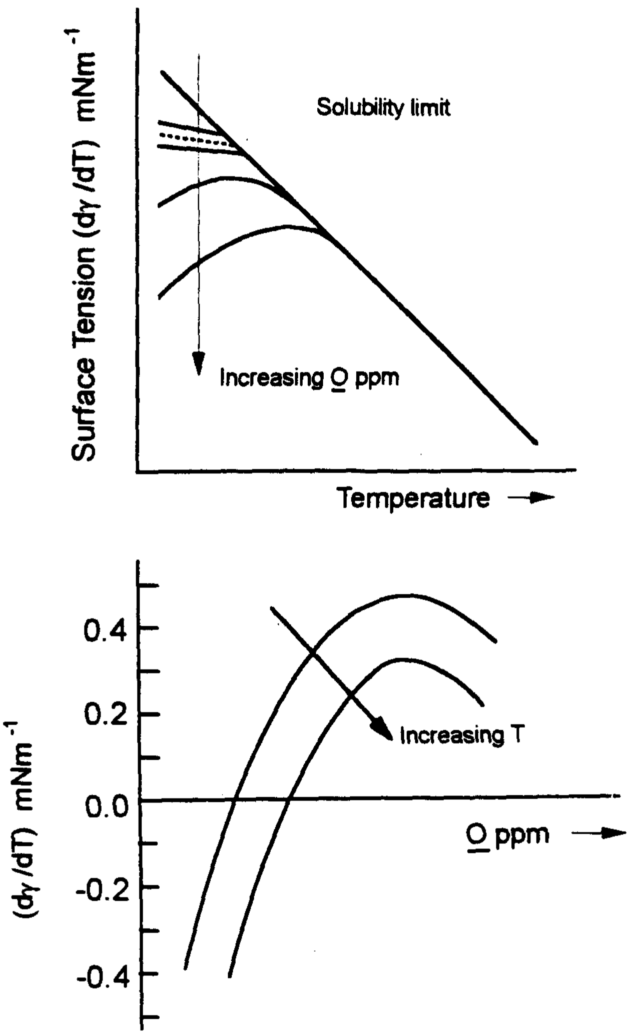


Figure 3 Schematic diagrams showing the effect of (a) both O̲ content and temperature on surface tension; - - - denotes saturation limit of O in metal and (b) on the temperature coefficient.

The general form of the surface tension of metals as functions of soluble O (or S) content and temperature is shown in Figure 3. It can be seen that:

(i) Surface tension decrease markedly with O̲ content.
(ii) The temperature coefficient (dγ/dT) changes from negative to positive with increasing O̲% and goes through a maximum (this change in sign in (dγ/dT) results in a change of direction of Marangoni, thermocapillary flows) which can have a substantial effect on the process e.g. single crystal growth, welding etc).
(iii) In some metals there is a relatively small oxygen solubility and this limits the effect of O̲ e.g. (dγ/dT) may remain negative but will diminish with increasing O̲; this seems to be the case with silicon. There is little point in developing novel and accurate techniques for surface tension

measurements on reactive metals if equal intention is not given to control and measurement of either the O content in the metal or the oxygen partial pressure above the melt.

Oscillating drop method

The oscillating drop technique has been widely used in recent years to measure surface tensions of reactive melts at high temperatures because there is no contamination of the melt from the container. The surface tension can be calculated from the relation (Equation 1) where m is the mass and $\omega_R$ is the Rayleigh frequency. However, the electromagnetic forces used to levitate and heat the specimen result in frequency spectrum with 3 or 5 peaks. The electromagnetic forces effectively augment the surface tension and result in (a) a high apparent value for surface tension ($\gamma_{app}$) and (ii) a mass dependence of $\gamma_{app}$. Cummings[32] derived the relation shown in Equation 2 for correcting for the electromagnetic forces using the translational frequencies ($\omega_{tr}$) of the drop.

$$\gamma = 3\pi m\,\omega_R^2 \qquad (1)$$

$$\omega_R^2 = \frac{1}{5}\sum \omega_1^2+\omega_2^2+\omega_3^2+\omega_4^2+\omega_5^2 - \omega_{tr}^2\left(1.9+\frac{0.6g}{r(2\pi\omega_{tr})^2}\right)^2 \qquad (2)$$

where g is the gravitational constant and r is the radius of the drop and subscripts 1 to 5 indicate the various individual peaks.

Surface tension measurements on gold were obtained with the oscillating drop method in terrestrial and micro-gravity conditions, the frequency spectra in microgravity showed a single peak and the value of the surface tension obtained was in excellent agreement with that derived in the terrestrial experiments[13]. Thus the Cummings relation (Equation 2) is considered to be an accurate method of correcting $\gamma$ for electromagnetic forces. This work carried out by Egry et al[16] is a classical example of how microgravity experiments should be carried out to provide definitive values for physical properties. Recently Rhim et al[14] have proposed a method for correcting surface tension for the effect of electrostatic forces.

Oxide films on the surface of an oscillating drop damp out all oscillations and prevent the determination of surface tension. It is possible to make measurements if the oxide film melts but caution must be applied in these conditions since 7 and 9 peak spectra may be obtained and it is necessary to take all peaks into consideration in Equation 2 to obtain reliable values for surface tension[33].

New techniques

Two novel techniques have been reported, both used on molten silicon and both could be classified as non-intrusive. In the dynamic hanging drop method the oscillations of a silicon drop on the bottom end of a graphite rod are determined whilst the rod is rotated at a known velocity ($\Omega$ = ca 600 rpm) of similar magnitude to the natural frequency of the drop (Figure 4). The surface tension was calculated by making measurements of the oscillation frequency ($\omega$) through a frame by frame analysis of the images obtained with a digital high speed camera. The measurements were carried out at two or more rotational speeds and the surface tension determined by Equation 3.

$$\gamma = \frac{\omega_2\Omega_1^2 - \omega_1\Omega_2^2}{\omega_1 - \omega_2}\, r^3\, F \qquad (3)$$

where $\omega$ = frequency, $\Omega$ = rotation speed, r = radius of drop and F = factor to account for the effect of density on the oscillation frequency. The authors[34] claim the major problem lies in the accurate alignment of the rod. They point out that a period of 3.5 seconds from the initiation of rotation was required for the establishment of sinusoidal oscillation.

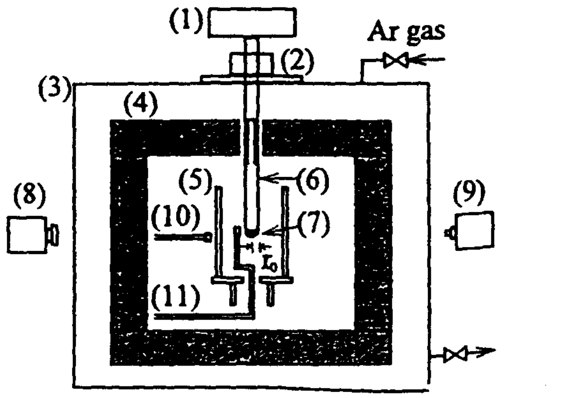


Figure 4 Schematic diagram showing the dynamic hanging drop apparatus. (i) speed control motor, (2) vacuum shaft, (3) main chamber, (4) insulation, (5) carbon heater, (6) carbon rod, (7) hanging drop, (8) high speed camera, (9) IR thermometer, (10) thermo-couples.

The surface laser-light scattering (SLLS) method was used[5] to study the *ripplon* on a liquid surface (Figure 5). Liquid surfaces at equilibrium may appear to be smooth but they are being continually deformed by thermal fluctuation of the molecules. Waves (called ripplons) have small amplitude (ca 1 nm) and wavelengths of ca 100 μm depending upon the frequency. Ripplon action is dependent upon surface tension for restoration and kinematic viscosity ($\nu = \eta/\rho$) for oscillation damping. The spectrum of ripplon was obtained with a Fourier spectrum analyser (providing the peak frequency $\omega_0$ in relation to the angular frequency and the full width at half maximum $2\Gamma$. The surface tension ($\gamma$) and dynamic viscosity were obtained from the Equations 4 and 5, respectively.

$$\gamma = \omega_o^2 \rho / k^3 \quad (4)$$

$$\nu = \Gamma / 2k^2 \quad (5)$$

where k is the wavenumber.

The results obtained with both the dynamic hanging drop and SLLS methods are in good agreement with results obtained using other techniques.

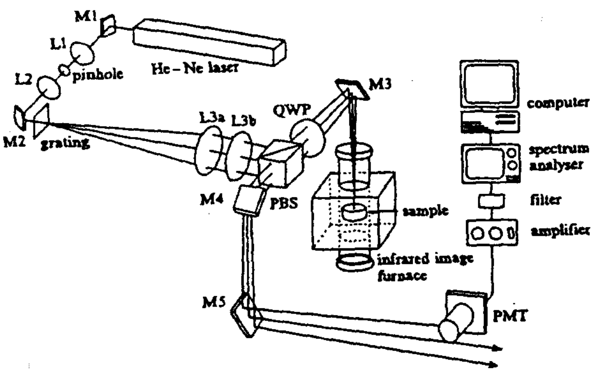


Figure 5 Schematic diagram showing SLLS method.

Conventional methods

The sessile drop method is dependent upon the use of the Young-Laplace equation; the recent introduction of algorithms to determine the surface tension (and density) from drop profile coordinates has helped to improve the accuracy of the results.

## 5. Properties Related to Heat Flow

### 5.1 Heat capacity ($C_p$), enthalpy ($\Delta H$)

Levitation methods

Levitated drop calorimetry has been used for measuring enthalpies and enthalpies of fusion ($\Delta H^{fus}$) for many high melting metals. Margrave et al[25] used electromagnetic levitation to measure $\Delta H^{fus}$ values for many refractory metals including W (mp 3422 °C i.e. 3695 K) where laser heating was used to augment electromagnetic induction heating. Rionchi[25] used acoustic levitation to determine enthalpies for W and $Al_2O_3$. The problems with levitated drop calorimetry lie in (i) uncertainties in temperature arising from uncertainty in emissivity and (ii) the need to differentiate enthalpy-temperature curves to obtain $C_p$ which can be particularly difficult if there is a high temperature phase transition (which is frequently the case with commercial materials).

Techniques using levitation[14] and microgravity[17] have been used to determine values for the ratio of ($C_p$/emissivity) from cooling curves in high vacuum. However, in general, the need for emissivity data is greater than that for $C_p$.

Subsecond Methods

Pulse or explosive wire methods[6,7,27] which use very rapid heating (10 $Ks^{-1}$) have been used to obtain $C_p$, ($H_T$-$H_{25}$) and $\Delta H^{fus}$ values for both solid and liquid phases. The experimental values have been found to be in good agreement with values obtained by conventional methods. However, values of $C_p$ for the solid may be prone to error where the material undergoes phase transformations at high temperature.

Conventional Methods

Differential scanning calorimetry has been extended to direct heat capacity measurement for molten metals for temperatures up to 1500 °C (1773 K) using an $Al_2O_3$ plaque to hold the specimen in a Pt crucible[36]. Values obtained on Ni indicated that measured $C_p$ values agreed with recommended values within an uncertainty band of ± 4% and were frequently within ± 2%[35].

### 5.2 Thermal diffusivity (a) and conductivity ($\lambda$)

The major problems in thermal diffusivity (a) and conductivity ($\lambda$) measurements lie in the determination of the magnitude of the contributions from convection and radiation conduction (for semi-transparent media) to the effective thermal conductivity ($\lambda_{eff}$) or diffusivity. For optically thick conditions, Equation 6 can be assumed, where the

$$\lambda_{eff} = \lambda_L + \lambda_{conv} + \lambda_R \quad (6)$$

subscripts L, conv, and R refer to the lattice, convective and radiation conduction, respectively. Silicon is semi-transparent in its solid state but is non-transparent in the liquid state.

It is exceedingly difficult to eradicate convection from *steady-state* measuring methods (such as the concentric cylinder method) usually carried out on liquid metals using transient techniques such as the hot wire (or line source) method or the laser pulse method.

Hibiya and co-workers[2,36,44] have attempted to eliminate convective contributions by

(i) Using electromagnetic forces to oppose convection on Hg[36].
(ii) carrying out measurements on liquid InSb using drop shaft and sounding rocket[2], the other workers[44] have used the traditional way of ensuring that the top of the molten specimen is hotter than the bottom to minimise the most convection.

Non-Intrusive Methods

The laser pulse (or flash) method has become the most widely-adopted technique for obtaining thermal diffusivities or conductivities. It is a robust technique and measurements on metals are usually completed in a time period of < 1 second, thereby minimising convective contributions. Experimental uncertainties of $\pm 5\%$ are usually assigned to measurements on solids. Measurements on liquid metals are usually carried out using sapphire ($Al_2O_3$) or $SiO_2$ cells which are transparent to infra-red radiation. Measurements have been carried out on Si[1)] and on other metals Fe, and commercial alloys[33)]. The results obtained in some cases show a divergence of 20-30% which may arise for one of the following reasons:

(i) convective contributions to the thermal diffusivity
(ii) the loss of disc-shaped geometry as a result of non-wetting conditions (the value of a is proportional to $L^2$ where L is the specimen thickness).
(iii) and to a lesser extent the formation of an oxide film which could introduce a thermal resistance at the surface.

Some differences in the laser pulse measurements may arise from the treatment of the temperature transient.

The establishment of reliable values for thermal diffusivity of liquid metals with high melting points will be an area of considerable activity in the next few years.

There have been several non-intrusive techniques used for measurements on low temperature systems but these have not yet been applied to high temperature systems; typical examples are:

(i) photothermal deflection[37)], (ii) laser-induced thermal grating[38)], (iii) thermal radiation calorimetry[39)], (iv) phase-sensitive techniques[40)], (v) photon-correlation spectroscopy, (vi) thermal wave measurements[41)], (vii) photo-acoustic[42)], (vii) laser-induced plasma[43)] and electron-beam methods[8)] (the latter has been used extensively for measurements on high-melting metals[8)]).

Line Source Method

The line source (or hot wire) method is widely used for measurements on non-conducting liquids at lower temperatures. However, there are few measurements on liquid metals because of the difficulty of electrically-insulating the wire or strip from the metal. Hibiya and Nakamura[44)] successfully insulated a thin metallic strip for measurements on molten InSb around 600 °C. They showed the magnitude of conventional contributions by making both measurements in microgravity and on earth. Convection was found to be initiated at times > 1 second. Yamasue, Susa et al[45)] obtained values on solid and molten Si using a $SiO_2$ coating on a Pt wire. The principal advantage of this technique is that convectional effects can be diagnosed by a departure from linearity in the plot of temperature change (of the wire) as a function of ln (time). Natamura et al[36)] used electromagnetic forces to suppress convection in measurements on mercury.

Wiedemann-Franz-Lorenz (WFL) Rule

It has been shown[46)] that thermal conductivities calculated for both solid and liquid near the melting point by the WFL Rule, ($\lambda = 2.45 \times 10^{-8}\ \sigma\ T$) lie within experimental error for most metals. This is also the case for silicon. This finding is particularly useful for calculating the thermal conductivities of alloys in the (solid + liquid) region since measurements of thermal conductivity (or diffusivity) tend to be in error due to the fact that some of the energy is used for further melting of the sample.

5.3 Electrical Conductivity ($\sigma$)

Egry and co-workers[18)] used a contactless method to measure electrical conductivities in microgravity.

Subsecond, rapid heating techniques have been used to derive electrical conductivity values for the solid and liquid states of refractory metals and commercial alloys[7,27)].

The 4-wire probe still continues to be used, two sets of measurements have been reported on silicon[1)]. There was a 7% variation in the results reported which may reflect contamination from the crucible and the electrodes.

5.4 Emissivity ($\varepsilon$)

The principal problems with emissivity measurements result from (i) stray radiation from shields etc and (2) roughness of the surface.

Levitation Methods

Measurements of spectral emissivities of molten levitated drops have been determined[22)] using electromagnetic levitation and rotating-analyser ellipsometry to determine the polarisation state of light reflected from the sample at various angles.

Recently, Watanabe et al[22)] used electromagnetic cold crucible levitation to determine emissivities of solid and molten silicon by comparison of the normal spectral radiance emitted by the sample with that by a blackbody. Two spectroscopes covering the range 200-2500 nm were used[22)]. Rhim et al[14)] derived values of the ratio of ($C_p$/ total normal emissivity, $\varepsilon_{TN}$) of Si by monitoring the cooling curves from a drop levitated electrostatically.

Non-Intrusive Techniques

Subsecond, rapid heating methods have been used to determine the spectral emissivities of metals, alloys and commercial alloys[7)]. Values were obtained for the liquid phase before the collapse of the wire sample.

## 6 Conclusions

(1) There has been a move to the use of levitation and reduced gravity conditions to minimise the problems of contamination of the melt from container/sample reactions and these have been applied to the measurement of all properties.

(2) Several novel non-intrusive techniques have been developed such as the dynamic hanging drop and surface laser-light scattering method for surface tension.

(3) In the case of surface tension measurements on reactive metals it is absolutely essential to both control and monitor the concentration of oxygen and any other surface active species.

(4) There is a need for some agreement on the analytical treatment used to (a) derive viscosity from damping data and (b) account for non-wetting conditions.

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