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Laser Ultrasonic Investigations
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A Dissertation

Presented to

the Faculty of the School of Engineering and Applied Science

University of Virginia

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy (Materials Science and Engineering)

by

Douglas Ted Queheillalt

January 2000
Approval Sheet

This Dissertation is submitted in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy, Materials Science and Engineering

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Abstract

The many difficulties associated with the growth of premium quality CdTe and (Cd,Zn)Te alloys has stimulated an interest in the development of a non-invasive ultrasonic approach to monitor critical growth parameters such as the solid-liquid interface position and shape during vertical Bridgman growth. This sensor methodology is based upon the recognition that in most materials, the ultrasonic velocity (and the elastic stiffness constants that control it) of the solid and liquid phases are temperature dependent and an abrupt increase of the longitudinal wave velocity occurs upon solidification.

The laser ultrasonic approach has also been used to measure the ultrasonic velocity of solid and liquid Cd$_{0.96}$Zn$_{0.04}$Te as a function of temperature up to 1140°C. Using longitudinal and shear wave velocity values together with data for the temperature dependent density allowed a complete evaluation of the temperature dependent single crystal elastic stiffness constants for solid and the adiabatic bulk modulus for liquid Cd$_{0.96}$Zn$_{0.04}$Te. It was found that the ultrasonic velocities exhibited a strong monotonically decreasing function of temperature in the solid and liquid phases and the longitudinal wave indicated an abrupt almost 50% decrease upon melting.

Because ray propagation in partially solidified bodies is complex and defines the sensing methodology, a ray tracing algorithm has been developed to analyze two-dimensional wave propagation in the diametral plane of cylindrical solid-liquid interfaces. Ray path, wavefront and time-of-flight (TOF) projections for rays that travel from a source to an arbitrarily positioned receiver on the diametral plane have been calculated and com-
pared to experimentally measured data on a model liquid-solid interface. The simulations and the experimental results reveal that the interfacial region can be identified from transmission TOF data and when used in conjunction with a nonlinear least squares reconstruction algorithm, the interface geometry (i.e. axial location and shape) can be precisely recovered and the ultrasonic velocities of both solid and liquid phases obtained with errors of less than ~ 3%.

To evaluate the sensor and gain insight into the melting and solidification process, a single zone VB growth furnace was integrated with the laser ultrasonic sensor system and used to monitor the melting and solidification characteristics of Cd$_{0.96}$Zn$_{0.04}$Te. The ultrasonic TOF signals indicated that the melting of Cd$_{0.96}$Zn$_{0.04}$Te was quite sluggish and that solidification was accompanied by a 10°C - 15°C undercooling. This behavior has been attributed to a combination of the low thermal conductivity and high heat capacity of this alloy in addition to constitutional supercooling effects.
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No! Try not.

Do. Or do not.

There is no try.

- Yoda
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<td>148</td>
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</tbody>
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# List of Symbols

**Symbol** | **Physical Property** | **Units**
--- | --- | ---
$\alpha$ | Amplitude attenuation per wavelength | (dB/s)
$\alpha$ | Thermal expansion coefficient | (1/K)
b | Bulk or volume viscosity (poise) | (g/cm s)
$C_p$ | Specific heat capacity | (J/g K)
c | Elastic stiffness tensor | (Pa)
$C_{ij}$ | Elastic stiffness tensor components | (Pa)
$\chi^2$ | Chi squared merit function | $(s^2)$
d | Particle displacement vector | (m)
$\delta_{ij}$ | Kronecker delta | unit-less
$E$ | Young’s modulus | (Pa)
$G$ | Shear modulus | (Pa)
h | Interfacial convexity | (mm)
k | Thermal conductivity | (W/cm K)
k | Wave number | (1/m)
$K$ | Bulk modulus | (Pa)
$K_S$ | Adiabatic bulk modulus - liquid phase | (Pa)
$L_m$ | Path length | (m)
$\Delta l/\ell_o$ | Linear thermal expansion | (%)  
$M_T$ | Thermoelastic modulus | (Pa)
n | Unit propagation vector | (m)
$\eta$ | Dynamic or shear viscosity (stokes) | (cm$^2$/s)
$\omega$ | Angular frequency | (1/s)
$\omega_v$ | Characteristic frequency | (1/s)
P | Pressure | (Pa)
$\mathbf{R}$ | Plane wave reflection coefficient | unit-less
$R_c$ | Radius of curvature | (mm)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
<td>Cylinder radius</td>
<td>(mm)</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Density - solid phase</td>
<td>(g/cm$^3$)</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>Density - liquid phase</td>
<td>(g/cm$^3$)</td>
</tr>
<tr>
<td>$\sigma_{CRSS}$</td>
<td>Critical resolved shear stress</td>
<td>(MPa)</td>
</tr>
<tr>
<td>$T$</td>
<td>Plane wave transmission coefficient</td>
<td>unit-less</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>($^\circ$C or K)</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
<td>($^\circ$C or K)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>(s)</td>
</tr>
<tr>
<td>$\tau_m$</td>
<td>Time of flight</td>
<td>(s)</td>
</tr>
<tr>
<td>$\theta_{liq}$</td>
<td>Ray propagation angle</td>
<td>($^\circ$ or rad)</td>
</tr>
<tr>
<td>$\theta_{long}$ or $\theta_l$</td>
<td>Ray propagation angle</td>
<td>($^\circ$ or rad)</td>
</tr>
<tr>
<td>$\theta_{shear}$ or $\theta_s$</td>
<td>Ray propagation angle</td>
<td>($^\circ$ or rad)</td>
</tr>
<tr>
<td>$\mathbf{u}(x, t)$</td>
<td>Particle velocity</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
<td>unit-less</td>
</tr>
<tr>
<td>$v$</td>
<td>Phase velocity</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$v_g$</td>
<td>Group velocity</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$v_{head}$</td>
<td>Head wave velocity</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$v_{liq}$</td>
<td>Phase velocity - liquid phase</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$v_{long}$ or $v_l$</td>
<td>Longitudinal wave velocity</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$v_{shear}$ or $v_s$</td>
<td>Shear wave velocity</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$v_{so}$</td>
<td>Zeroth-order Lamb wave velocity</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$v_{sol}$</td>
<td>Phase velocity - solid phase</td>
<td>(m/s)</td>
</tr>
<tr>
<td>$x, y, z$</td>
<td>Displacement</td>
<td>(m)</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Solid-liquid interface position</td>
<td>(mm)</td>
</tr>
<tr>
<td>$z_r$</td>
<td>Laser receiver position</td>
<td>(mm)</td>
</tr>
<tr>
<td>$z_s$</td>
<td>Laser source position</td>
<td>(mm)</td>
</tr>
<tr>
<td>$Z$</td>
<td>Acoustic impedance</td>
<td>(g/cm$^2$ s)</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Overview of CdTe Crystal Growth

Single crystal cadmium telluride (CdTe), Fig. 1.1, and substitutional solid solution Cd$_{1-y}$Zn$_y$Te alloys (with $0.03 < y < 0.05$) are used for solid state γ-ray detectors and as substrate materials for the epitaxial growth of Hg$_{1-x}$Cd$_x$Te (with $x = 0.2$) thin film infrared focal plane array (IRFPA) sensors [1-5]. As the size of imaging detectors continues to increase, a need has emerged for large area ($>4 \times 6$ cm$^2$) Cd$_{1-y}$Zn$_y$Te high quality substrates with low defect (i.e. dislocation and Te precipitate) densities, a uniform Zn distribution and high infrared transmission coefficient. Although CdTe and (Cd,Zn)Te alloys are currently grown by vapor and liquid phase processes, these alloys are predominantly grown from the melt. These crystals have been grown by various techniques including zone refining, [6-8] vertical gradient freeze, [9-11] liquid encapsulated Czochralski (LEC) methods, [12-14] horizontal (HB) and vertical (VB) Bridgman techniques [15-20]. Due to variable yields, none of these methods have demonstrated reliable growth of material with the quality needed for today’s infrared (IR) detector applications [3].
Figure 1.1 Equilibrium phase diagram for Cadmium Telluride (CdTe) [21].

The size of imaging detectors (i.e. the number of pixels) and their individual performance depends on the quality of the substrate [22-24]. Commercial production of CdTe and (Cd,Zn)Te substrates are predominantly grown from the melt using the vertical variant of the Bridgman process (VB), Fig. 1.2. During VB solidification the bulk ingot is first compounded from its elements in a pyrolitic boron nitride (PBN) liner contained in a sealed cylindrical quartz ampoule placed in the furnace hot zone (~1120°C). The furnace is slowly translated so that the compounded charge passes through a thermal gradient into a cold zone (~750°C) resulting in directional solidification of a crystalline semiconductor [25-28]. A seed is typically not used for CdTe and CdZnTe growth and so a polycrystalline boule, dominated by a few large grains, is obtained. The quality and size of substrates is determined by the subsequent success of “mining” 〈111〉 oriented wafers for IRFPA and γ-ray detector applications.
Figure 1.2 A seven zone vertical Bridgman (VB) crystal growth furnace (with separate cell for Cd overpressure control) used for growing of (Cd,Zn)Te crystals.
CdTe ingots grown in this manner tend to be polycrystalline even when a seed crystal is used and growth of the large diameter single crystals is not common. One reason is that among all semiconducting compounds which crystallize in the cubic zinc blende structure, Fig. 1.3, CdTe has the lowest defect activation energy (i.e. stacking fault energy) associated with the formation of twin lamallae [29]. In addition, the high ionicity (~74%) of CdTe appears to increase the propensity for twin formation when compared with other III-V and II-VI compounds [29]. In most cases, secondary grains and growth twins appear to nucleate at the liquid-solid interface or at the surface of the boule where the freezing interface is in contact with the boron nitride or quartz growth ampoule. Secondary grains, once formed, tend to grow both inward and enlarge. One possible explanation for such behavior is the shape of the liquid-solid interface. It is believed that the optimum shape of the solid surface at the liquid-solid interface is slightly convex, a situation which should force surface related defects to grow radially outward [27]. Conversely, a concave interface may promote inward growth of surface related defects and secondary grains. Non-planar interfaces also have radial gradients of temperature. Differential expansion results in the formation of sheer stresses and the generation of dislocations is quite common because of the low critical resolved shear stress ($\sigma_{CRSS}$) of CdTe near its melting point [30]. Also, a Cd overpressure cell is often used (because of its high vapor pressure at the melting point) to prevent the precipitation of Te upon solidification and cooling [31].

Small additions of Zn (3 - 5 at.%) to stoichiometric CdTe has been shown to reduce both the dislocation density and the number of subgrain boundaries [32,33]. A 4% addition of Zn has also been shown to decrease the dislocation density an order of magnitude (from $10^5$ to $10^4$ cm$^{-2}$) and increase the yield strength 8-fold [34]. It also results in better lattice matching to subsequent epitaxial deposition of Hg$_{1-x}$Cd$_x$Te [34-36]. Addition of 4 at.% Zn to CdTe provides a lattice mismatch between epitaxial Hg$_{0.8}$Cd$_{0.2}$Te (MCT)
and Cd$_{0.96}$Zn$_{0.04}$Te of only 0.02% [15] and thus a low incidence of misfit dislocations and reduced epilayer strain in the MCT [37,38].

These observations have led to the recognition that during crystal growth many factors including the solid-liquid interface growth velocity and the shape of the solid-liquid interface, together with local temperature gradients control the mechanism of solidification (planar, cellular or dendritic), the likelihood of secondary grain nucleation/twin formation (i.e. the loss of single crystallinity), solute (dopant) segregation, dislocation generation, etc. and therefore determine the resultant crystals' quality, Fig. 1.4 [39]. For crystals grown by the vertical variant of the Bridgman (VB) technique, it is believed the optimum (Cd,Zn)Te properties are obtained with a low (~1 - 5 mm/hr) constant solidification velocity and a planar or near planar (slightly convex toward liquid) interface shape maintained throughout growth [1,10].

(Cd,Zn)Te - Zince Blende Structure

![Diagram of Cd,Zn)Te - Zinc Blende Structure]

Figure 1.3  A schematic illustration of the cubic zinc blende structure, (Cd,Zn)Te.
Figure 1.4 A schematic illustration showing the representation of the many physical phenomena incurred during liquid phase bulk crystal growth [25].
The solidification rate and interface shape are sensitive functions of the internal temperature gradient (both axial and radial) during solidification which are governed by the heat flux distribution incident upon the ampoule, the latent heat release at the interface, and heat transport (by a combination of conduction, buoyancy and surface tension driven convection, and radiation) within the ampoule [40-42]. Uncertainties in their thermophysical properties and the complexity of the theoretical transport process make it difficult to predict the exact location of the interface. Because the interface is contained within an opaque liner in the furnace at \(\sim 1150^\circ\text{C}\) it is not possible to visually identify the location either. The solid-liquid interface’s instantaneous location, growth velocity and interfacial shape during growth are therefore difficult to observe or predict, and optimization is difficult, especially for those semiconductor materials with low thermal conductivity such as CdTe and its alloys [1]. The result is that the yield of premium quality single crystal substrates obtained in this manner is limited by the current capabilities of the vertical Bridgman growth process and are typically about 10% [43]. The development of non-invasive sensor technologies to detect and monitor the solid-liquid interface position and shape over time during VB crystal growth have become recognized as an important next step for developing a better understanding of the growth process.

1.2 Motivation for Ultrasonic Sensing

The many difficulties associated with the growth of premium quality CdTe and (Cd,Zn)Te alloys has stimulated an interest in the development of both invasive and non-invasive approaches to monitor critical growth parameters such as the solid-liquid interface position and shape during VB growth. Many have suggested that an ultrasonic transmission based approach be investigated. This sensing methodology is based upon the recognition that in most materials, the ultrasonic velocity (and the elastic stiffness con-
stants that control it) of the solid and liquid phases are temperature dependent and an abrupt increase of the longitudinal wave velocity occurs upon solidification [44-46].

For example, silicon and germanium are two semiconductors for which extensive solid and liquid elastic constant and density (i.e. ultrasonic velocity) data exists in the literature. The temperature dependence of the longitudinal wave velocity for Si and Ge has been evaluated from the density [47] and elastic stiffness [48-51] data. Figure 1.5 shows that the longitudinal wave velocity is a relatively strong monotonic function of temperature in the solid and liquid phases and exhibits an abrupt drop (of between 40 and 55% depending on the crystallographic orientation of the solid) upon melting.

This abrupt velocity increase upon solidification, will cause the time-of-flight (TOF) of ultrasonic pulses that propagate through a sample to increase when it melts. Ultrasonic rays that propagate through the interface region during solidification are therefore likely to be sensitive to the instantaneous position and shape of the solid-liquid interface. The measurement of the time-of-flight for sets of ultrasonic rays that traverse the region might be combined with reconstruction algorithms to determine critical growth parameters such as the solid-liquid interface position, interface shape and local velocity fields (which are related to local thermal gradients).
1.3 Scope of this Dissertation

The ultrasonic study of solidification has been pursued for many years in other materials systems. However, its application to CdTe has been precluded by the extreme difficulty of making physical contact with a sample contained in a pyrolitic boron nitride liner inside a sealed quartz ampoule which is buried inside a furnace at ~1150°C. The recent emergence of laser ultrasonics (i.e. laser generation and interferometric detection) now offer the possibility of non-invasively introducing laser based ultrasonic source and receivers into high temperature crystal growth furnaces. This work attempts to develop and evaluate potential laser ultrasonic sensor methodologies capable of in-situ monitoring the melting-solidification characteristics of a representative Cd$_{0.96}$Zn$_{0.04}$Te sample.
Ray propagation in partially solidified bodies is complex and defines the sensing methodology. To aid in the sensors development, a bench top laser ultrasonic system has been developed to measure TOF projection data of rays penetrating model isotropic solid-liquid interface configurations. A combination of ray path, TOF and wavefront analysis was used to fully characterize potential sensing configurations for three interface shapes (convex, planar and concave). These experiments indicated that fan-beam TOF projection data sets reveals significant information about the solid-liquid interface’s position and interface height. In addition, a nonlinear least-squares reconstruction algorithm was developed to quantitatively recover the solid-liquid interface position, the interface height and the local velocity fields in the solid and liquid phases.

The integration of this sensor technology into a prototype VB growth furnace required a priori knowledge of the ultrasonic velocities for the crystal. Therefore the single crystal elastic stiffness constants for the solid phase and adiabatic bulk modulus for the liquid phase of Cd$_{0.96}$Zn$_{0.04}$Te have been evaluated from TOF data collected in primary low index crystal orientations. Using the elastic stiffness data together with data for the temperature dependent density allowed a quantitative analysis of the waveforms obtained with this sensor system.

To evaluate the sensor and gain insight about the solidification process a single zone VB growth furnace was integrated with the laser ultrasonic sensor system and used to monitor the melting and solidification characteristics of Cd$_{0.96}$Zn$_{0.04}$Te ingots. This laser ultrasonic sensor attempts to provide new insights into the growth process and promise to motivate new sensor and modeling activities related to the growth of CdTe alloys. Due to the fact that ultrasonic sensors may provide “real time” data, it offers the possibility of new sensor based process control technologies for in-situ monitoring and direct feedback control of vertical Bridgman growth technologies.
Chapter 2

Interfacial Demarcation Methodologies

Interface demarcation \textit{(i.e.} determination of the solid-liquid interface position and shape\textit{)} as a function of time during growth can be classified either by destructive or non-destructive analysis. This chapter reviews the state of the art (both destructive and non-destructive) for interface demarcation and assesses their relevance for the VB solidification of (Cd,Zn)Te alloys. The development of such sensors to measure critical growth parameters such as the solidification rate and the solid-liquid interface shape during growth is expected to lead to a better understanding of the physical processes occurring during solidification.

2.1 Destructive

Solid-liquid interface measurements by the destructive approach has been around for many years. The simplest method for examining a liquid-solid interface is to rapidly quench a partially solidified sample, slice it in the axial plane and examine it by metallography. The obvious drawback to these testing procedures is the fact that they are destructive, \textit{i.e.} the crystal is destroyed or irreversibly damaged during evaluation. It is difficult to
apply to VB growth of CdTe because the samples are polycrystalline and therefore not easy to see the interface, the low thermal conductivity makes it hard to rapidly quench and the high partial pressure of Cd at the melting point makes it very dangerous. During destructive testing the growth process may be interrupted as with decanting [52] or quenching [20,53,54]. A less destructive approach uses mechanical pulsing [55,56] or radioactive tracer [57] experiments.

Huang et al. [52] used decanting methods to determine the solid-liquid interface shape during vertical Bridgman growth of CdGeAs$_2$. During solidification, growth was interrupted and the melt was merely poured off the partially solidified crystal. After decanting, the partially solidified crystal was sliced longitudinally along the growth axis, polished and etched to reveal the solid-liquid interface position and shape. Although decanting reveals the interface shape clearly, this method is very difficult with semiconducting materials such as CdTe which are normally grown in evacuated quartz ampoules.

Capper et al. [53] and Huang et al. [54] have used quenching methods to determine the solid-liquid interface shape during vertical Bridgman growth of (Hg,Cd)Te and (Pb,Sn)Te, respectively. During solidification, growth was perturbed and the melt was frozen in by quenching the partially solidified crystal in either air or water. After quenching, the crystal was sliced longitudinally along the growth axis, polished and etched to reveal the solid-liquid interface position and shape. The solid-liquid interface position and shape was marked by the different microstructural features of the VB solidified and quenched microstructures. Because of the low thermal conductivity ($k = 1 \times 10^{-2}$ W/cmK) and high heat capacity ($C_p = 150$ J/gK) of CdTe such a “thermal shock” is not capable of freezing in the interface shape [1]. However, a stable growth condition is very sensitive to the redistribution of solute atoms at the solid-liquid interface. Consequently a small excess (3 - 4 at.%) of Te in a CdTe melt was used to produce a constitutional supercooled zone by
Pfeiffer et al. [20]. The infraction of the criterion of constitutional supercooling allowed the interface shape to be sharply visible due to the redistribution of solute atoms.

Although these destructive methods are accurate and where applicable quite reliable, they can only be used to determine the solid-liquid interface position and shape at one particular moment of time during growth. Therefore, many growth runs would have to be used to evaluate the position and shape along the entire ingot length and this could prove to be quite costly for expensive semiconducting materials such as CdTe.

To circumvent the "single use" nature of the previous methods mechanical pulsing has been used to mark the interface [55,56]. During Czochralski growth of InSb single crystals (doped with Te) the ampoule was mechanically pulsed, which induced impurity vibrational striations along the solid-liquid interface. Again, the crystals were sliced longitudinally along the growth axis, polished and etched to reveal the solid-liquid interface position and shape with good results.

In a similar method, during VB solidification of CdTe doped with radioactive indium, ($^{111}$In) growth was sharply speeded up which resulted in a band with higher concentrations of $^{111}$In frozen in at the solid-liquid interface [57]. The crystals were sliced longitudinally along the growth axis, polished and autoradiography was used to reveal the solid-liquid interface position and shape with good results.

2.2 Non-Destructive

Interest in non-invasive sensor technologies to monitor the growth process include X-ray radiography [57-62], eddy-current techniques [63-75] and ultrasonics [76-81]. They are potentially applicable to any semiconductor system and would perhaps facilitate direct on-line control of solidification parameters such as growth velocity, interfacial shape and
thermal gradients. Each of these sensor methodologies relies on the existence of a significant difference in one or more material properties between the solid and liquid phases at the melting point. For instance, the density difference is utilized for X-ray radiography and the electrical conductivity change for eddy-current sensing. For ultrasonic sensing, the variation in the elastic compressibility is used.

2.2.1. X-ray Radiography

The intensity, \( I \), of an X-ray transmitted through a material over a distance \( l \) can be described by \( I = I_0 \exp(-\alpha l) \) where \( I_0 \) is the initial X-ray intensity and \( \alpha \) is the absorption coefficient [60]. The absorption coefficient \( \alpha \) is constant for a material and dependent on atomic number. Therefore, it can be inferred that for a material with a fixed composition, \( \alpha \) is dependent on temperature because thermal expansion reduces the number of atoms per unit length. In addition, most materials exhibit an expansion or contraction upon solidification (a change in the density also results in a change in the number of atoms per unit length) and thus the solid and liquid phases of many semiconductors will possess different X-ray absorption coefficients. Table 2.1 shows the absolute and relative difference between the solid and liquid phases for a few semiconductor systems. This difference in the X-ray absorption coefficients between the solid and liquid phases provides high-contrast visualization of the solid-liquid interface for some semiconductor materials.

X-ray radiography has been used for both diameter measurement [58] and solid-liquid interface demarcation [59,60] during liquid encapsulated Czochralski (LEC) and vertical Bridgman-Stockbarger (VBS) growth [61,62] of elemental and compound semiconductors. To observe the solid-liquid interface using X-ray radiography, a crystal growth furnace must be modified with an X-ray image processing system, generally consisting of an X-ray source and detector with an image processor, Fig. 2.1. Because of the
high absorption of the furnace containment and the small differences in the absorption coefficients of solid and liquid semiconductors the signal-to-noise (S/N) ratio is low and image processing techniques must be applied to achieve the necessary resolution needed for monitoring semiconductor crystal growth.

This technique can provide reasonable detection of the solid-liquid interface to within a few mm resolution provided the relative difference between the absorption coefficients (hence density) of the solid and liquid phase is sufficiently large. During X-ray radiography of Czochralski grown GaP crystals (density difference ~5%), the solid-liquid interface was not observed, and only diameter control was successful [58]. Where during LEC growth of GaAs [59] and Si [60]; and VB growth of InSb [61,62], the density difference was on the order of 10%, and the solid-liquid interface was observed. It is clear from Table 2.1 that the very small changes in density makes X-ray radiography an unsuitable methodology for determining the solid-liquid interface position and shape during growth of CdTe and its Zn containing alloys.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Point $T_m$ (°C)</th>
<th>Solid Density $\rho_s$ (g/cm$^3$)</th>
<th>Liquid Density $\rho_l$ (g/cm$^3$)</th>
<th>$\rho_s - \rho_l$ (100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si [47]</td>
<td>1410</td>
<td>2.30</td>
<td>2.53</td>
<td>+10.0</td>
</tr>
<tr>
<td>GaAs [47]</td>
<td>1237</td>
<td>5.16</td>
<td>5.71</td>
<td>+10.7</td>
</tr>
<tr>
<td>InSb [47]</td>
<td>525</td>
<td>5.76</td>
<td>6.48</td>
<td>+12.5</td>
</tr>
<tr>
<td>GaP [59]</td>
<td>1477</td>
<td>---</td>
<td>---</td>
<td>+5.5</td>
</tr>
<tr>
<td>CdTe [63]</td>
<td>1098</td>
<td>5.74</td>
<td>5.67</td>
<td>-1.2</td>
</tr>
</tbody>
</table>
Figure 2.1 Schematic illustration of a liquid encapsulated Czochralski (LEC) crystal growth chamber with integrated X-ray radiography system [59].

2.2.2. Eddy-Current Techniques

The electrical conductivities of selected solid and liquid semiconductor's at their melting points are given in Table 2.2. Table 2.2 shows that for selected semiconductors, the electrical conductivity of the liquid is many times that of the solid at the melting point. Therefore non-invasive eddy current methods offer a means of sensing it and thus locating the liquid-solid interface. Eddy current techniques use a sinusoidally varying an alternating current applied to a coil placed near the sample to induce a changing electromagnetic field within a test object [64,65]. In conductive materials change to this electromagnetic field induces eddy currents in the material. These eddy currents in turn create a secondary electromagnetic field. The strength of the secondary field is indicative of the conductivity
field within the material. It can be monitored by measuring the induced voltage in a pick-
up coil placed near the sample. Eddy current sensing techniques have been used to moni-
tor thermal gradients (both axial and radial) during Czochralski growth of Si [66,67] and
in the case of vertical Bridgman growth a combination of extensive finite element model-
ing [69-72] and in-situ sensing [68,72-75] have been used to successfully monitor the
solid-liquid interface during growth of (Cd,Zn)Te alloys. These techniques are most sensi-
tive to the solidification interface near the outside of a sample. The skin effect limits the
extent of penetration of the fields beneath the sample surface. For example, the skin depth
is on the order of 10 mm at 100 kHz in solid CdTe and on the order of 2 mm at 100 kHz
for liquid CdTe at its melting temperature [72].

Stefani et al. [66] and Choe et al. [67] developed a computer controlled eddy cur-
rent system for in-situ monitoring Czochralski single crystal growth of silicon. Their
experimental design used a single coil eddy current sensor which was scanned along the
solid crystal to obtain the electrical conductivity data, which was converted to temperature
values and thermal profiles with reasonable accuracy. However, there was no attempt to
monitor the solid-liquid interface position or shape because the sensor was only positioned
in the already solidified crystal.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_s$</th>
<th>$3.0\times10^4$</th>
<th>$5.8\times10^4$</th>
<th>$1.25\times10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_l$</td>
<td>6600</td>
<td>$7.9\times10^5$</td>
<td>$1.2\times10^6$</td>
<td>$1.4\times10^6$</td>
</tr>
<tr>
<td>$\sigma_l/\sigma_s$</td>
<td>5.5</td>
<td>26.3</td>
<td>20.7</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Table 2.2: The electrical conductivities of selected solid ($\sigma_s$) and liquid ($\sigma_l$)
semiconductors close to their melting points [47,71].

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To fully investigate eddy current sensor methodologies, Dharmasena et al. [69,70] and Wadley et al. [71] have used extensive electromagnetic finite modeling methods to investigate the design of both an “absolute” and a “differential” eddy current sensor for monitoring the solid-liquid interface position and interface curvature during the vertical Bridgman growth of semiconducting materials. It was found that GaAs was most suited for eddy current sensing because of its high liquid electrical conductivity and large liquid:solid conductivity ratio. For semiconductor systems of similar (or higher) conductivity ratios, the absolute or differential sensor methodologies can be used to discriminate the solid-liquid interface position to better than ±0.5 mm [71]. Less suited systems such as CdTe, require the exploitation of fringe fields at the ends of the excitation coil together with a differential sensing scheme to achieve similar interfacial location precision. Once the solid-liquid interface’s position is obtained, lower frequency data can also be used to deduce the interfacial curvature with acceptable precision for both high and low liquid:solid conductivity ratio semiconductor systems [71].

These eddy current sensor principles were integrated into the ceramic liner of a commercial 17-zone vertical Bridgman growth furnace and used to monitor the nucleation [72,73] and growth [74,75] of Cd_{0.96}Zn_{0.04}Te crystals, Fig. 2.2. Unlike the single coil sensor of Stefani et al. [66] and Choe et al. [67] the absolute and differential sensors were maintained at a fixed location with respect to the ampoule and used to monitor melt cooling/composition [72,73], observe nucleation [72,73], detect the position of the liquid-solid interface [74,75], measured the interfacial curvature [74,75] and determined the electrical resistivity of the solid during post solidification annealing [72,73]. These experimental studies confirmed earlier predictions that a two coil, multifrequency sensor approach can independently recover the liquid-solid interface position and provide insight about its curvature during VB growth of (Cd,Zn)Te alloys [75]. However, these eddy current tech-
niques are best used for "seeing" the liquid-solid interface near the surface, therefore making detection near the axis of the sample (where the eddy current density approaches zero) difficult [72-75]. In addition, other factors such as buoyancy driven convection flows in the liquid can effect the eddy current sensors response [72-75].

Figure 2.2 Schematic diagram of a 17-zone vertical Bridgman furnace with an integral two coil eddy current sensor [72-75].

2.2.3. Ultrasonics

Ultrasonic sensing methodologies are based on the difference in elastic stiffness and density between the solid and liquid phases. In general, most materials exhibit both an expansion (i.e. a density reduction) and a decrease in their elastic stiffness during melting. These ultrasonic techniques can be categorized as either pulse-echo where ultrasound is generated and reflections are detected by the same transducer element or pitch-catch where ultrasound is generated and detected by different transducers. Several groups have
sought to apply these methods to the solidification of metals and semiconductor systems [76-78].

One ultrasonic approach to solid-liquid interface sensing has sought to exploit the acoustic impedance difference across the interface using a pulse-echo method to detect ultrasonic reflections from the interface. This approach has been investigated by Parker et al. [76] for Si, Jen et al. [77] for Ge and Carter et al. [78] also for Ge as a means for identifying the position of solid-liquid interface during vertical Bridgman solidification, Fig. 2.3.

At a solid-liquid interface, the energy of the incident wave is partitioned between the reflected and refracted waves. The energy partition is governed by the acoustic impedance \( Z_i = \rho v_i \), where \( \rho \) is the density and \( v_i \) is the respective velocity. The normal-incidence plane wave reflection coefficient \( (R) \), which is the ratio of reflected beam intensity \( (I_r) \) to incident beam intensity \( (I_i) \), at a planar solid-liquid interface is a function of the impedance difference across the interface [79]:

\[
R = \frac{I_r}{I_i} = \left( \frac{Z_{sol} - Z_{liq}}{Z_{sol} + Z_{liq}} \right)^2
\]

where \( Z_{sol} \) and \( Z_{liq} \) are the acoustic impedances of the solid and liquid phases, respectively. The normal-incidence plane wave transmission coefficient \( (T) \), which is the ratio of transmitted beam intensity \( (I_t) \) to incident beam intensity \( (I_i) \), at a planar liquid-solid interface can also be described in terms of the acoustic impedance [79]:

\[
T = \frac{I_t}{I_i} = \left( \frac{4Z_{sol}Z_{liq}}{(Z_{sol} + Z_{liq})^2} \right)^2.
\]
It is assumed that all of the acoustic energy is either reflected or refracted and therefore $R + T = 1$. Also, the reflection and transmission coefficients are the same whether the acoustic energy is incident upon a solid-liquid or liquid-solid interface.

Table 2.3 shows the longitudinal wave velocities and densities of the solid and liquid phases for various semiconductors at their respective melting point and the calculated reflection and transmission coefficients. It is clear, from Table 2.3, that relatively weak reflections arise when ultrasound is normally incident upon these semiconductor solid-liquid interfaces. Therefore, sensor methodologies which exploit transmission coefficients may be preferable.

![Schematic diagram of a vertical Bridgman growth furnace with a pulse-echo ultrasonic sensing system.](image-url)
In each of these investigations ultrasound was generated piezoelectrically from either the cold or hot end of the cylindrical sample. They measured the time-of-flight (TOF) for signals reflected from the solid-liquid interface to determine the interface position. However, large poorly characterized axial temperature gradients introduced uncertainties in mapping TOF data into interface axial position and little information could be inferred about interfacial curvature by this method.

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<tr>
<td>V</td>
<td>5.13</td>
<td>4.99</td>
<td>4.52</td>
<td>8.60</td>
<td>8.37</td>
<td>7.63</td>
<td>3.71</td>
<td>3.59</td>
<td>3.20</td>
<td>3.02</td>
<td>2.94</td>
<td>2.62</td>
</tr>
<tr>
<td>%h</td>
<td>2.71</td>
<td>2.71</td>
<td>2.71</td>
<td>3.92</td>
<td>3.92</td>
<td>3.92</td>
<td>2.67</td>
<td>2.67</td>
<td>2.67</td>
<td>1.34</td>
<td>1.34</td>
<td>1.34</td>
</tr>
<tr>
<td>%r</td>
<td>47.2%</td>
<td>45.7%</td>
<td>40.0%</td>
<td>54.4%</td>
<td>53.2%</td>
<td>48.7%</td>
<td>27.9%</td>
<td>25.5%</td>
<td>16.4%</td>
<td>55.6%</td>
<td>54.4%</td>
<td>48.9%</td>
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<tr>
<td>T</td>
<td>5.26</td>
<td>5.26</td>
<td>5.26</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
<td>5.76</td>
<td>5.76</td>
<td>5.76</td>
<td>5.74</td>
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</tr>
<tr>
<td>%r</td>
<td>5.51</td>
<td>5.51</td>
<td>5.51</td>
<td>2.53</td>
<td>2.53</td>
<td>2.53</td>
<td>6.48</td>
<td>6.48</td>
<td>6.48</td>
<td>5.67</td>
<td>5.67</td>
<td>5.67</td>
</tr>
<tr>
<td>%r</td>
<td>0.083</td>
<td>0.076</td>
<td>0.052</td>
<td>0.110</td>
<td>0.102</td>
<td>0.077</td>
<td>0.011</td>
<td>0.008</td>
<td>0.001</td>
<td>0.152</td>
<td>0.144</td>
<td>0.108</td>
</tr>
<tr>
<td>%r</td>
<td>0.917</td>
<td>0.924</td>
<td>0.948</td>
<td>0.890</td>
<td>0.898</td>
<td>0.923</td>
<td>0.989</td>
<td>0.992</td>
<td>0.999</td>
<td>0.848</td>
<td>0.856</td>
<td>0.892</td>
</tr>
</tbody>
</table>
In an alternative approach, one can to exploit the ultrasonic delay when rays are partially transmitted through the lower velocity liquid. Mauer et al. [80] and Norton et al. [81] have reported measurement of the TOF for rays transmitted through a solid-liquid interface during the controlled solidification of polycrystalline aluminum, Fig. 2.4. In their experiments, the samples were stationary and their outer surface never exceeded 650°C and so a combination of laser generated ultrasound and waveguide coupled piezoelectric transduction was used to make the measurements. Because extensive a priori knowledge about the interface was available they were able to construct an interface model (with a small number of unknown coefficients) and could use a simple ray tracing code to compute predicted TOF values for rays propagating between the known source and receiver points. In these studies, the rays were incident normal to the interface and ray refraction was minimal. A nonlinear least-squares method was able to reconstruct the interface shape from the small (10) ray path data set. When a priori information is less abundant, ultrasonic tomographic techniques using convolution backprojection algorithms have also successfully recovered velocity distributions from laser ultrasonic TOF projection data [82,83]. In these situations, significantly more TOF values are needed, and the approach has not been extended to situations where ray bending is significant.
Figure 2.4 Schematic diagram of the laser ultrasonic/waveguide coupled piezoelectric transduction sensing system used for monitoring the directional solidification of aluminum [80].
Chapter 3

Principles of Ultrasonic Propagation

The principles upon which ultrasonic sensing of solidification processes is founded are beginning to become well established. The concepts underlying of ultrasonic wave propagation in liquids and solids and the interactions of these waves with solid-liquid interfaces are reviewed below together with ultrasonic ray theory. Emerging laser methods for conducting ultrasonics (i.e. laser generation and detection of ultrasound) are then examined.

3.1 Ultrasonic Wave Propagation

Ultrasonic disturbances of small amplitude propagate as linear elastic waves whose propagation through a body results in particle oscillations about their equilibrium positions. In ideal liquids and gases only one propagation mode exists. This longitudinal mode has particle displacements parallel to the direction of ultrasonic propagation. The ultrasonic velocity is governed by the materials compressibility and for these materials, is independent of propagation direction. Elastic solids can accommodate transverse waves (where particle displacements are perpendicular to the direction of propagation) as well as
longitudinal waves. The particle motions in elastic solids associated with these three bulk modes of propagation can be resolved into three perpendicular components, one longitudinal and two transverse to the direction of propagation. The theory of linear elastic wave propagation in both liquids [84,85] and solids [86-88] have been widely reviewed. A brief review of wave propagation principles applicable to laser ultrasonic sensing is presented below.

3.1.1 Wave Propagation in Liquids

When an ultrasonic wave propagates through a liquid the density, pressure and temperature of an infinitesimal element of liquid vary periodically with time. In ideal (non-viscous, non-absorbing) liquids, the pressure/density cycle due to propagation of an ultrasonic wave takes place adiabatically or at constant entropy [84,85]. With these assumptions a plane harmonic wave (i.e., longitudinal wave) propagates unattenuated and with a frequency independent velocity that is determined by the liquids compressibility from the thermodynamic equations of state [85].

In the case of non-ideal liquids, the liquid may exhibit either viscous or absorption effects, i.e. some of the ultrasonic energy is dissipated (by local heating) and the wave attenuates in amplitude with propagation. In this case the ultrasonic velocity becomes frequency dependent (dispersive propagation). This non-ideal wave propagation can be described by Navier-Stokes equation of hydrodynamics (in the acoustic approximation):

\[ \rho_o \frac{\partial^2 \mathbf{u}(x,t)}{\partial t^2} = \rho_o \frac{\delta P}{\delta \rho} \frac{\partial^2 \mathbf{u}(x,t)}{\partial x^2} + \left( b + \frac{4}{3} \eta \right) \frac{\partial}{\partial t} \left( \frac{\partial^2 \mathbf{u}(x,t)}{\partial x^2} \right) \]  \hspace{1cm} (3.1)

where \( \mathbf{u}(x,t) \) is the particle velocity, \( \rho_o \) is the density of the liquid in the absence of the sound wave, \( \delta P \) and \( \delta \rho \) are the changes in the pressure and density due to \( \mathbf{u}(x,t) \), \( b \) is the
bulk or volume viscosity and $\eta$ is the dynamic or shear viscosity \[85\]. Assuming one-dimensional plane harmonic wave propagation ($u_1$ is a function of $x_1$ only, $u_2 = u_3 = 0$), $\delta P/\delta \rho = K_S/\rho_o$ where $K_S$ is the adiabatic bulk modulus. By defining a characteristic frequency $\omega_v = K_S(b + (4/3)\eta)^{-1}$ a dispersion equation may be expressed as

$$k^2 = \omega^2 \left(\frac{\rho_o}{K_S}\right) \frac{1}{1 + i\omega/\omega_v}. \tag{3.2}$$

Since $\omega$ is real, $k$ can take complex values, $k = k_1 - ik_2$, where $k_1$ and $k_2$ are both real and positive, and solving for a plane wave propagating in the $x_1$-direction, the longitudinal wave phase velocity can be expressed in the form:

$$v = \frac{\omega}{k_1} = \frac{2K_S}{\rho_o} \frac{\sqrt{\left[1 + (\omega/\omega_v)^2\right]}}{1 + \left[1 + (\omega/\omega_v)^2\right]^{1/2}}, \tag{3.3}$$

where the amplitude attenuation per wavelength can be expressed as:

$$\alpha = \frac{2\pi v k_2}{\omega} = \pi \left(\frac{\nu^2 \rho_o}{K_S}\right) \frac{\omega/\omega_v}{1 + (\omega/\omega_v)^2}. \tag{3.4}$$

As $b$ and $\eta \to 0$ and/or $\omega \ll \omega_v$ (i.e. MHz region for non-viscous liquids), the longitudinal wave phase velocity, $v_{liq}$, approaches that of an ideal liquid and is given by

$$v_{liq} = \frac{K_S}{\rho}. \tag{3.5}$$

As an initial assumption $b$ is allowed to approach zero and viscous effects are due to $\eta$ only \[88\]. Substituting values of $K_S = 10.17$ GPa and $\eta = 2.5$ cp for liquid $Cd_{0.96}Zn_{0.04}Te$ at $1100^\circ\text{C}$ into $\omega_v = K_S(b + (4/3)\eta)^{-1}$ the characteristic frequency is
approximately 300 GHz. Figures 3.1 and 3.2 show the deviation from ideality (Eqns. (3.5 and (3.6)) for the longitudinal wave phase velocity and the *amplitude attenuation per wavelength* for liquid Cd$_{0.96}$Zn$_{0.04}$Te at 1100°C as the normalized frequency $\omega/\omega_v$ is increased. It is clear from Fig. 3.1 that the range of frequencies generated from laser based ultrasonics ($< 3$ MHz) falls in the linear portion of the curve. Therefore ideal behavior is assumed and the longitudinal wave phase velocity does not deviate from Eqn. (3.5). Although the *amplitude attenuation per wavelength* does deviate from ideality in this range of frequencies, the attenuation is small until the frequency exceeds 3 GHz.

![Graph](image)

**Figure 3.1**  The deviation from ideality of the longitudinal wave phase velocity vs. the normalized frequency for liquid Cd$_{0.96}$Zn$_{0.04}$Te at 1100°C.
Figure 3.2  The deviation from ideality of the \textit{amplitude attenuation per wavelength} vs. the normalized frequency for liquid Cd$_{0.96}$Zn$_{0.04}$Te at 1100°C.
3.1.2 Wave Propagation in Solids

In elastic solids each of the three modes has its own characteristic velocity, although in isotropic solids the two transverse velocities are degenerate. For anisotropic solids the phase velocity ($\nu$) of the three possible bulk wave modes (quasi-longitudinal, fast and slow quasi-shear) in a direction defined by the unit propagation vector, $\mathbf{n}$, with components $n_j$, $j = 1,2,3$ can be found from the eigenvalues of the Christoffel equation [88]:

$$ (k^2 c_{ijkl} n_k n_l - \rho \omega^2 \delta_{ij}) d_j = 0, \quad i = 1,2,3 $$

(3.6)

where $\rho$ is the density, $k = \omega \nu$ is the wave number, $\omega$ is the angular frequency, $c_{ijkl}$ are the components of the elastic stiffness tensor, $d_j$, $j = 1,2,3$ are the components of the unit particle displacement vector, $\mathbf{d}$, and $\delta_{ij}$ is the Kronecker delta [88]. For a given propagation direction vector $\mathbf{n}$, the squares of the phase velocities of the bulk modes are obtained as the eigenvalues of Eqn. (3.6). The particle displacement vector $\mathbf{d}$ of a bulk mode is obtained as a unit eigenvector for the phase velocity (eigenvalue) of the bulk mode. The slowness (or inverse velocity) surface gives the inverse phase velocity as a function of propagation direction and is independent of $\omega$. Some useful properties of the slowness surface are examined below.

An important consequence of anisotropic wave propagation is that the energy of a wave packet does not necessarily propagate parallel to the wave propagation direction [88]. In a lossless medium, the energy¹ or group velocity is perpendicular to the slowness surface. The power flow angle (defined as the angle between the energy velocity and the propagation direction, $\kappa$) depends on the shape of the slowness surface and therefore

---

¹. It is assumed that waves propagate in a lossless medium and the terms energy and group velocity are therefore used interchangeably.
changes with crystallographic orientation. The group velocity, which governs the speed of a modulated disturbance \(i.e.\) a pulse, can be determined once the phase velocity and the displacement vector for a specific mode are known. The Cartesian components of the group velocity, \(v_g\), are then obtained from [88]

\[
v_g = \frac{c_{ijk}dFdN_k}{\rho v}, \quad i = 1,2,3. \tag{3.7}
\]

Equation (3.7) may be greatly simplified for propagation in high-symmetry directions, where the phase and group velocities are equal [88].

The most straightforward and precise method for evaluating the elastic stiffness constants of anisotropic solids is through the measurement of the ultrasonic velocity of pure longitudinal and pure shear modes propagating in principal symmetry directions, \(i.e.\) in the \(\langle 100\rangle\), \(\langle 110\rangle\) and \(\langle 111\rangle\) for cubic materials. Cadmium telluride and its substitutional solid solution (Cd,Zn)Te alloys crystallize in a zinc-blende (cubic) structure. It can be shown from Eqn. (3.6) and (3.7) that the three bulk wave velocities (one longitudinal and two shear) can be expressed as a function of the elastic stiffness constants \(C_{11}, C_{12}, C_{44}\) and the density \(\rho\). Table 3.1 gives the expressions for the pure longitudinal and pure shear velocities in the primary \(\langle 100\rangle\), \(\langle 110\rangle\) and \(\langle 111\rangle\) directions for a cubic crystal structure. Note, that the two shear wave velocities are equivalent in both \(\langle 100\rangle\) and \(\langle 111\rangle\) directions. Moreover, it can be shown that in all cases in Table 3.1, except for the shear wave in the \(\langle 111\rangle\) direction, the energy flux vector is in the same direction as the wave normal [88].
Table 3.1: Relationships between elastic constants and ultrasonic velocities for cubic materials.

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Longitudinal</th>
<th>Shear</th>
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<tr>
<td>$C_{11}$</td>
<td>$\sqrt{\frac{C_{11}}{\rho}}$</td>
<td>$\sqrt{\frac{C_{44}}{\rho}}$</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>$\sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}}$</td>
<td>$\sqrt{\frac{C_{11} - C_{12}}{2\rho}}$</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>$\sqrt{\frac{C_{44} - C_{12}}{3\rho}}$</td>
<td>$\sqrt{\frac{C_{11} - C_{12} + 2C_{44}}{3\rho}}$</td>
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<tr>
<th>Orientation</th>
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<tr>
<td>(100) in plane</td>
<td>$V_l$</td>
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<tr>
<td>(110) in plane</td>
<td>$V_s$</td>
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<tr>
<td>(110) in plane</td>
<td>$V_{ls}$</td>
</tr>
<tr>
<td>(111) in plane</td>
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<tr>
<td>(111) in plane</td>
<td>$V_s$</td>
</tr>
</tbody>
</table>
Velikov and Rusakov [89] report that cadmium telluride (a cubic crystal) has three independent elastic stiffness constants: \( C_{11} = 53.30 \) GPa, \( C_{12} = 36.50 \) GPa and \( C_{44} = 20.44 \) GPa while the density equals \( 5.854 \) g/cm\(^3\) at 20°C [90]. Bulk cubic single-crystal materials for electronic applications are usually grown with a low index crystallographic orientation such as \( \langle 100 \rangle \), \( \langle 110 \rangle \) or \( \langle 111 \rangle \). Using the elastic constants of Velikov and Rusakov, Figs. 3.3 - 3.5 show the calculated phase velocity, slowness and group velocity surfaces for the three bulk modes on the \( \{001\} \), \( \{110\} \) and \( \{111\} \) planes of CdTe, respectively.

On the \( \{001\} \) planes the quasi-longitudinal group velocity is greatest in \( \langle 110 \rangle \) directions and the smallest in \( \langle 100 \rangle \) directions. On \( \{110\} \) planes the velocity is greatest in \( \langle 111 \rangle \) direction and smallest in \( \langle 001 \rangle \) directions; minimal anisotropy is present on the \( \{111\} \) plane for the quasi-longitudinal mode. The cusps on the quasi-shear curves of Fig. 3.5 arise from the convoluted form of the quasi-shear slowness curve, Fig. 3.4, on the vicinity of high symmetry directions [88]. This is due to the fact that there are two wave vectors (near the vicinity of each high symmetry direction) that correspond to energy flow along the high symmetry direction. it follows that these two wave vectors must have the same energy velocity as the wave propagating in the high symmetry direction. No cusps are observed for the pure shear mode of Fig. 3.5(a) because the slowness surface is a sphere and the energy or group velocity is parallel to the wave propagation direction, \( k \).

Details of the algorithm developed to solve for the phase and group velocities can be found in Appendix A.
Figure 3.3  Phase velocity surfaces for cadmium telluride on the (a) \{001\}, (b) \{110\}, and (c) \{111\} planes assuming $C_{11} = 53.30$ GPa, $C_{12} = 36.50$ GPa, $C_{44} = 20.44$ GPa and $\rho = 5.854$ g/cm$^3$ at 20°C.
Figure 3.4  Slowness surfaces for cadmium telluride on the (a) {001}, (b) {110}, and (c) {111} planes assuming \( C_{11} = 53.30 \) GPa, \( C_{12} = 36.50 \) GPa, \( C_{44} = 20.44 \) GPa and \( \rho=5.854 \) g/cm\(^3\) at 20°C.
Figure 3.5  Group velocity surfaces for cadmium telluride on the (a) {001}, (b) {110},
and (c) {111} planes assuming $C_{11} = 53.30 \text{ GPa}$, $C_{12} = 36.50 \text{ GPa}$, $C_{44} = 20.44 \text{ GPa}$ and $\rho = 5.854 \text{ g/cm}^3$ at 20°C.
3.2 Reflection/Transmission at a Liquid-Solid Interface

When an ultrasonic wave propagating in a homogeneous medium passes through an interface at a normal incident angle where the velocity (i.e. elastic stiffness and density) of the second medium is different (i.e. solid-solid or solid-liquid interface) the incident wave is reflected and transmitted without any change in propagation direction. However when an ultrasonic wave propagating in a homogeneous medium passes through an interface at a non normal incident angle the incident wave is mode converted (a change in the nature of the wave motion) and refracted (a change in direction of wave propagation) [91-95]. These phenomena may affect the entire beam or only a portion of the beam and the sum total of the changes that occur at the interface depends on the angle of incidence and the velocity of the ultrasonic waves leaving the point of impingement on the interface [79]. Figure 3.6 shows a diagram of the relationship of possible reflected and refracted waves of an incident longitudinal wave in a liquid impinging on a solid interface.

The reflection and refraction of these ultrasonic waves is governed by the acoustic analog of Snell’s law (the ratio of the sine of the angle of incidence to the sine of the angle of reflection or refraction equals the ratio of the corresponding wave velocities):

\[
\frac{\sin \theta_{\text{liq}}}{v_{\text{liq}}} = \frac{\sin \theta_{\text{l}}}{v_{\text{l}}} = \frac{\sin \theta_{\text{s}}}{v_{\text{s}}} = \frac{\sin \theta_{\text{head}}}{v_{\text{head}}} \tag{3.8}
\]

where \(\theta_{\text{liq}}, \theta_{\text{l}}, \theta_{\text{s}}\) and \(\theta_{\text{head}}\) are the ray propagation angles (with respect to the surface normal) and \(v_{\text{liq}}, v_{\text{l}}, v_{\text{s}}\) and \(v_{\text{head}}\) are the velocities of the longitudinal wave in the liquid, the longitudinal, shear and the head wave\(^1\) in the solid.

---

\(^1\) A head wave is a wave which propagates at a liquid - solid interface.
Referring to Fig. 3.6, if the angle of incidence, $\theta_{\text{liq}}$, is small, the incident wave undergoes a mode conversion at the liquid-solid interface, resulting in the simultaneous propagation of longitudinal and shear waves in the solid. If the angle $\theta_{\text{liq}}$ is increased, the direction of the refracted longitudinal wave will approach the plane of the liquid-solid interface, $\theta_{\text{long}} \to 90^\circ$. At the first critical incident angle, $\theta_{\text{long}} = 90^\circ$ and the refracted longitudinal wave will disappear, leaving only a refracted (mode converted) shear wave to propagate in the solid. If $\theta_{\text{liq}}$ is increased beyond this first critical angle, the direction of the refracted shear wave will approach the plane of the liquid-solid interface, $\theta_{\text{shear}} \to 90^\circ$. At this second critical incident angle, $\theta_{\text{shear}} = 90^\circ$ and the refracted shear wave will disappear and the incident wave is only reflected at an angle equal to the incident angle. This methodology can be applied to any interface (i.e. liquid-solid, solid-liquid, solid-solid).

Figure 3.6 A schematic illustration showing reflected, refracted and mode converted rays at a liquid-solid interface.
3.3 Ultrasonic Ray Theory/ Image Reconstruction

3.3.1 Ultrasonic Ray Theory

Geometrical acoustics or ray theory describes the propagation behavior of acoustic rays in liquid and solid bodies. In the development of an ultrasonic sensor methodology for reliable image reconstruction using refracted ray paths, the sometimes severe nature of ray bending implies a need for precise knowledge of ray paths if TOF data is to be used for image reconstruction. At the fundamental level, the measured time-of-flight, $\tau_m$, for an acoustic ray that propagates along a path of length $L_m$ is defined by

$$\tau_m = \int_{L_m} \frac{dl}{v}, \quad m = 1, 2, \ldots, M$$  \hspace{1cm} (3.9)

where $dl$ is an infinitesimal element of the path, $v$ is the ultrasonic velocity ($1/v$ is the local slowness) within the object and $M$ is the number of different rays.

In general there are two methods for determining the ray path between two points: shooting and bending. The shooting method uses an iterative procedure to determine the ray path from the source point by solving the differential equations that follow from ray theory for different initial conditions until the ray arrives at the receiver point [96-98]. Ray bending uses Fermat’s principle as a starting point; it tries to determine a ray path between two points by searching for the minimum travel-time between them [96-98].

Both methods have serious limitations. By shooting a fan of rays leaving the source, one can obtain an impression of the wave field. However, convergence problems are known to occur frequently, especially in three-dimensions. Also, shooting will not find diffracted ray paths or ray paths in shadow zones, where ray theory breaks down. With bending, one can find every ray path satisfying Fermat’s principle, even a diffracted one,
but only for one source-receiver pair at a time, and it is not certain whether the path has an absolute minimum travel-time or only a local minimum travel-time. The reader is referred to several comprehensive reviews on ray theory and ray tracing in isotropic and anisotropic materials by Moser [96-98], Andersen et al. [99] and Kline and Wang [100,101]. For the work contained within, both shooting and ray bending methods were used.

3.3.2 Image Reconstruction

Ultrasonic computerized tomography (CT) has been widely used in the fields of seismology and medicine. However, it has been finding recent applications in non destructive testing applications. It has been shown, Eqn. (3.9), that the time of flight of an individual ray path or raysum is the path integral of the ultrasonic slowness. A set of either parallel or fan-beam raysums encompassing an image is called a projection, Fig. 3.7. To reconstruct an object image from ultrasonic TOF projection data either convolution back-projection (CB) methods or algebraic reconstruction techniques (ART) are generally utilized [102,103].

Convolution backprojection methods have not been applied to situations where ray bending is significant, and although algebraic reconstruction techniques are beginning to incorporate ray bending [104], both these procedures require large data sets which may be difficult to obtain during crystal growth. Reconstruction approaches that can be used with limited data and exploit the often significant a priori information available are preferable.

The crystal grower requires only the axial location of the interface (its change with time gives the solidification velocity) and its approximate curvature. If the liquid and solid velocities could be also obtained, they might also be useful since they are related to the local temperature, composition and the crystals crystallographic orientation.
Figure 3.7 A schematic illustration showing a) parallel beam and b) fan beam projections, assuming no ray bending.

From this, an interface model can be constructed and a nonlinear least squares reconstruction approach can be applied for image reconstruction using ultrasonic TOF projection data.

In general, a nonlinear least squares reconstruction approach calculates an initial TOF projection set from the models trial solution and proceeds until the $\chi^2$ merit function stops or effectively stops decreasing. If the model to be fitted is represented by $\hat{\tau}_i = \hat{\tau}(x_i, a)$ then the $\chi^2$ merit function can be expressed by

$$\chi^2(a) = \sum_{i=1}^{M} \left[ \frac{\tau_i - \hat{\tau}(x_i, a)}{\sigma_i} \right]^2$$

(3.10)

where $\tau_i$ are the measured TOFs and $\hat{\tau}_i$ are the numerically simulated TOF's for each iteration, $M$ is the number of data points and $a$ is the matrix notation of the unknown parame-
ters [105]. If the uncertainty (σ) is unknown, as in this case, then it is assumed constant and equal to 1.

3.4 Laser Ultrasonics

Laser based ultrasonics, as described here, refers to laser generation and laser interferometric detection of ultrasound. In general, laser generation of ultrasound is based on the absorption of electromagnetic (light) energy and its conversion to acoustic (mechanical) energy. The laser ultrasonic approach emerged after the development of Q-switched lasers which allow the rapid deposition of significant electromagnetic energy on a surface and the resultant production of energetic elastic waves (ultrasound). Most laser ultrasonic detection systems are based on surface displacement interferometers. There have been many comprehensive reviews of laser generation of ultrasound in both liquids and solid such as Hutchins [106], Sigrist et al. [107,108], Lyamshev et al. [109,110] and Scruby et al. [111]. Monchalin [112] and Scruby et al. [111] have also presented reviews of laser detection of ultrasound.

3.4.1 Laser Generation of Ultrasound

Many physical processes occur when a surface is illuminated by a laser, including heating, generation of thermal waves, generation of elastic waves (ultrasound), and material may be ablated from the surface and a plasma formed. However our focus is the generation of elastic waves from laser illumination. Numerous mechanisms have been recognized as contributing factors to laser generation in both liquids and solids: including thermoelastic expansion, ablation (vaporization), surface melting, plasma formation, dielectric breakdown, electrostriction and radiation pressure [111]. However, the two dominant mechanisms for ultrasonic generation are thermoelastic expansion and ablation.
At low laser power densities (<$10^6$ W/cm$^2$) localized heating in the region of irradiation produces an elastic pulse by thermal expansion of the heated volume, Fig. 3.8(a). This thermoelastic expansion generates relatively strong forces parallel to the surface and a weak force normal to the surface, from thermal diffusion, thereby generating both longitudinal and shear waves.

At higher power densities (>$$10^8$$ W/cm$^2$) the incident laser pulse raises the surface temperature above the vaporization threshold and a small region of material is ablated, Fig. 3.8(b). During ablation, or vaporization in the case of liquids, atoms and small droplets are ejected from the surface at high velocities creating a transient a force normal to the surface and a large amplitude elastic impulse directed normal to the sample. This generates a strong longitudinal pulse normal to the surface. During ablation, the thermoelastic stresses, which would always accompany ablation, are negligible compared to the forces generated from ablation. Therefore, it would seem that ablation would be necessary to produce longitudinal waves of significant amplitude for non-destructive testing applications in applications where some surface damage is allowable.

However, large amplitude longitudinal waves are also generated during thermoelastic expansion if the surface is constrained with a thin layer of liquid between a transparent solid and the sample surface. This technique modifies the surface of the sample to introduce large stresses normal to the surface, which are otherwise minimal for the thermoelastic source at a free surface by three mechanisms; constraint of the solid, thermoelastic expansion of the liquid and constraint of the liquid itself. Thus the constrained surface source generates a sound field more akin to that of ablation, but at significantly lower power densities and with minimal surface damage. However, the need to constrain a surface in this manner reduces the usefulness of the laser ultrasonic source for many non-destructive testing applications.
Figure 3.8 A schematic illustration showing generation mechanisms incurred during laser generation; (a) thermoelastic expansion and (b) ablation.

3.4.2 Laser Detection of Ultrasound

Optical ultrasonic detection systems pose certain advantages over conventional detection systems (piezoelectric and electromagnetic acoustic transducers) in that they are non-perturbing to the crystal growth process. There are a variety of optical detection systems which can be employed for the detection of ultrasound; the knife edge technique, surface displacement interferometry and velocity interferometry [112]. Although laser interferometry is rather insensitive compared with piezoelectric devices, it offers a number of advantages including; easily translatable, no fundamental restriction on surface temperature, high spacial resolution and measurements may be localized over a few microns.

The optical detection of ultrasound can be accomplished interferometrically by collecting the light reflected (or scattered) from a surface as it is subjected to an ultrasonic disturbance, Fig. 3.9. Surface displacement interferometers interfere the scattered/ reflected light with a reference beam resulting in a measurement of the optical phase.
which is directly related to the instantaneous surface displacement. Most optical ultrasonic detection systems are based on surface displacement interferometers such as the Michelson or Mach-Zehnder type interferometer. The Mach-Zehnder heterodyne interferometer (as used here) uses a two beam system in which a single laser beam is split and frequency shifted (via a Bragg cell). In velocity interferometry, changes in the frequency of the scattered or reflected light are monitored and the doppler shift is used to measure velocity. Surface displacement interferometers (Michelson or Mach-Zehnder) are widely used at low frequencies with highly reflective surfaces whereas velocity interferometers offer higher sensitivities at high frequencies and do not require highly reflective surfaces.

![Image of wavefronts, diffusing surface, source, lens, and laser beam with a speckle pattern.](image)

**Figure 3.9** A schematic illustration showing optical detection via interferometry.
Chapter 4

Simulations of Ray Paths and Wavefronts

The geometric ray theory can be used to evaluate laser ultrasonic sensor configurations for monitoring the solid-liquid interface position and shape. This can also be complemented by experimental testing using an isotropic bench-top model system. Here, a combination of theoretical ray path and wavefront analysis of a model system (where the interface geometries are precisely known) was used to evaluate sensing configurations.

4.1 Model Solid-Liquid Interface

The bench-top model with known, solid-liquid velocities, consisted of water and solid polymethylmethacrylate (PMMA) contained in a cylindrical aluminum (2024-T6) “ampoule”. The interface convexities \( h \) (defined such that \( h > 0 \) corresponds to a convex interface and \( h < 0 \) a concave interface) examined here were \( h = \pm 2, \pm 5, \pm 10 \) mm and planar \( (h = 0 \text{ mm}) \). The aluminum ampoule had an inner radius of 75.0 ± 0.1 mm and an outer radius of 77.0 ± 0.1 mm. The water and PMMA were assumed to have longitudinal wave velocities of 1.50 ± 0.01 mm/\( \mu \)s and 2.67 ± 0.01 mm/\( \mu \)s at 21°C, respectively [90]. The
6061-T6 Al alloy had a measured longitudinal wave velocity of $6.35 \pm 0.01 \text{ mm/\mu s}$ and a shear wave velocity of $3.01 \pm 0.01 \text{ mm/\mu s}$ at 21°C.

4.2 Methodology

To simulate, it was first assumed that an infinitesimally wide, omnidirectional ultrasonic point source and receiver was positioned on the diametral plane. When an ultrasonic pulse was generated by the source, it was assumed to propagate in all directions, including the diametral plane. One of the directions (usually) results in a ray path (which may or may not be refracted, depending on the source and receiver’s relative positions) whose path connects the source and the receiver points. Determining this ray path is a necessary first step for understanding ultrasonic propagation through a solid-liquid interface, for predicting a ray’s TOF and ultimately, for attempting to reconstruct the interface position and shape from a TOF projection data set.

Consider the case where the source and receiver are both on the diametral plane. If the coordinates of the source $(x_s, z_s)$ and receiver $(x_r, z_r)$ points on the diametral plane are prescribed, then determining the ray path between these two points constitutes a boundary-value problem [113]. The solutions of boundary-value problems like this are usually preceded by solutions of initial value problems in which initial ray angles at the source point are prescribed and the ray paths obtained by solving for the refraction angles at the interface. After obtaining the ray paths for an arbitrary set of initial ray angles emanating from the source point, the ray path between a prescribed source and receiver point can be obtained using the shooting method [114]. In this approach, an initial ray direction is first arbitrarily chosen, and the distance between the receiver point and the intersection of the ray path with the outer boundary calculated. The procedure is then repeated using a slightly different initial ray angle until the distance is smaller than a prescribed tolerance $\delta$. 

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\((-1 \times 10^{-5}\) of the sample's diameter. The ray path and wavefront analysis used the initial value problem by specifying the source point and the initial ray angle. The solution for the boundary-value problem will be used in the next chapter for image reconstruction.

A further complication may arise during geometric ray tracing because acoustic energy can only be transmitted across an interface when the refraction angle is less than \(\pi/2\). This can sometimes lead to an incomplete projection data set with potentially deleterious consequences for some interface reconstruction techniques.

When an ultrasonic ray propagating in the diametral plane is incident upon an interface, both reflected and refracted rays propagate on the diametral plane (defined by the incident propagation vector and the normal to the interface at the intersection of the incident ray with the interface). Therefore, when ultrasonic sources are located in the diametral plane, rays propagated toward the interface tend to remain in the diametral plane. Here the diametral cross-sectional plane is arranged such that the plane in which ultrasonic rays propagate coincides with the \(x-z\) plane in a Cartesian coordinate system, Fig. 4.1. For the analysis here it is assumed that during crystal growth, the local thermal gradients in the region of propagation would be small and axially symmetric resulting in uniform velocities on both sides of the spherically shaped interface. The interface curvature (convex, planar, concave) is assumed to be a spherical cap with the center of curvature on the \(z\)-axis. On the diametral plane the interface is defined as a segment of a circle of radius \(R_c\). If the cylinder radius is denoted by \(R_s\), the interface height by \(h\), the interface radius \(R_c\) is given by

\[
R_c = \frac{R_s^2 + |h|^2}{2|h|}.
\] (4.1)
The origin of the coordinate system is chosen such that when \( h = 0 \) the interface is contained in the \( x-y \) plane, Fig. 4.1.

It is assumed that the omnidirectional ultrasonic source generates ray paths in all directions. One possible mode of propagation generates a ray path in the ampoule from the source point \((x_s, z_s)\) to the receiver point \((x_r, z_r)\), Fig. 4.2. This encircling wave propagates with a velocity equal to the zeroth-order symmetric Lamb wave [115]. In thin film and shell samples, Lamb waves are the preferred mode of propagation and the \( s_o \) mode is indicative of the highest velocity and lowest frequency component of these modes. Although Lamb waves are dispersive, as the frequency-thickness product approaches zero, the velocity of the lowest order mode approaches a value independent of frequency, \( v_{so} \). This zeroth-order Lamb wave velocity for the symmetric mode is represented by

\[
v_{so} = \sqrt{\frac{E}{\rho (1 - \nu^2)}} \tag{4.2}
\]

where \( E \) is Young's modulus, \( \nu \) is Poisson's ratio and \( \rho \) is the density. Using experimentally determined values for Young's modulus and Poisson's ratio of 66.4 GPa and 0.35, respectively along with a density of 2.70 g/cm\(^3\), the zeroth-order symmetric Lamb wave velocity for 6061-T6 is 5.30 mm/\( \mu \)s. This encircling wave offers one possibility of monitoring the average surface temperature of the ampoule because \( v_{so} \) is a function of temperature due to the fact that elastic properties (\( E \) and \( \nu \)) and the density (\( \rho \)) are a function of temperature.
Figure 4.1  Schematic illustrations of the coordinate systems used for (a) convex, (b) planar and (c) concave interface shapes.

Figure 4.2  A schematic illustration showing possible modes of diametral and encircling ray path propagation.
4.3 Convex Interface \((h > 0)\)

4.3.1 Source located in the liquid \((z_s > 0)\)

First consider a convex interface shape, and ray paths for prescribed source \((x_s, z_s)\) coordinates with initial ray angles \(\alpha\). On the diametral plane, the interface is defined by the equation for a circle of radius \(R_c\):

\[
R_c^2 = x^2 + [z + (R_c - |h|)]^2.
\]

The equation for a ray path (with initial ray angle \(\alpha\)) is

\[
z = \tan \alpha (x - x_s) + z_s.
\]

Suppose a source point is located in the liquid \((z_s > 0)\). The equation for the ray path that intersects the circle tangentially at \((x_0, z_0)\) and propagates only in the liquid without suffering refraction is given by

\[
x_0 x + [z_0 + (R_c - |h|)][z + (R_c - |h|)] = R_c^2.
\]

where the coordinates for the tangential point \((x_0, z_0)\) to the interface are given by

\[
x_0 = \frac{R_c^2 - [z_0 + (R_c - |h|)]z_s'}{x_s} \quad (4.6)
\]

\[
z_0 = \frac{R_c^2 z_s'}{x_s^2 + z_s'^2} + R_c \sqrt{\left(\frac{R_c z_s'}{x_s^2 + z_s'^2}\right)^2 - \frac{R_c^2 - x_s^2}{x_s^2 + z_s'^2}} - (R_c - |h|), \quad (4.7)
\]

where \(z_s' = z_s + (R_c - |h|)\).
For $z > 0$ and the initial ray angle $\alpha > \alpha_c$, all the rays propagate in the liquid along straight ray paths, where $\alpha_c = \tan(\Delta z_{eq}/x_{eq})$ is the critical angle at which the ray path touches the interface tangentially. When $\alpha < \alpha_c$, rays intersect the liquid-solid interface at $(x_1, z_1)$. Since the intersection point $(x_1, z_1)$ satisfies both Eqns. (4.3) and (4.4), it is obtained as one of two roots. Since the intersection point is to the left side of the tangential point $(x_0, z_0)$, the root with $x_1 < x_0$ was chosen.

The ray’s incident angle to the interface, $\theta_{\text{liq}}$, is defined as the angle between the normal to the interface at $(x_1, z_1)$ and the ray path given by Eqn. (4.4). The equation for the normal to the interface at $(x_1, z_1)$ can be written

$$x(z_1 + R_c - |h|) - x_1 z = 0. \tag{4.8}$$

The incident ray angle $\theta_{\text{liq}}$ is

$$\theta_{\text{liq}} = \tan \left[ \frac{x_1(x_1 - z_1) + z_1(z_1 - z_2)}{\sqrt{x_1^2 + z_1^2(z_1 - z_2)^2}} \right]. \tag{4.9}$$

The first refraction angle $\theta_{\text{sol}}$ at $(x_1, z_1)$ is calculated next. Since the incident ray propagates in the liquid with a constant velocity $v_{\text{liq}}$, the refraction angle $\theta_{\text{sol}}$ of the refracted ray in the solid can be determined simply using Snell’s law:

$$\theta_{\text{sol}} = \sin \left[ \frac{v_{\text{sol}}}{v_{\text{liq}}} \sin \theta_{\text{liq}} \right], \tag{4.10}$$

where $v_{\text{sol}}$ is the longitudinal velocity in the solid.

After the first refraction has occurred, the equation for the refracted ray path in the solid is

$$z = \cot(\phi_1 + \theta_s)(x - x_1) + z_1, \tag{4.11}$$
where \((\theta_2 + \phi_1 - \pi/2)\) is the angle between the refracted ray path and the \(x\)-axis and

\[
\phi_1 = \arctan \left( \frac{x_1}{z_1 + (R_e - |h|)} \right).
\]  

(4.12)

A second refraction may sometimes occur at a point \((x_2, z_2)\) on the solid-liquid interface. The point \((x_2, z_2)\) is again obtained as one of the two roots of Eqns. (4.3) and (4.4). Since the second intersection point is on the right side of the tangential point \((x_0, z_0)\), the root with \(x_2 > x_0\) was chosen. In the case where a second refraction does not occur at the solid-liquid interface, the root with \(z_2 < z_0\) was chosen.

The incident angle to the interface at \((x_2, z_2)\) is also equal to \(\theta_{sol}\). Since the longitudinal velocity in the liquid is assumed to be a constant \(v_{liq}\), the second refraction angle \(\theta_{2_{liq}}\) at \((x_2, z_2)\) can be determined simply using Snell's law:

\[
\theta_{2_{liq}} = \arcsin \left[ \frac{v_{liq}}{v_{sol}} \sin \theta_{sol} \right].
\]  

(4.13)

The doubly transmitted ray path is now totally defined by the source point \((x_s, z_s)\), the first and second interface intersection points \((x_1, z_1)\) and \((x_2, z_2)\) and the refraction angle \(\theta_{2_{liq}}\). Where the single transmitted ray path is defined by the source point \((x_s, z_s)\), the first intersection point \((x_1, z_1)\) and the refraction angle \(\theta_{sol}\).

Assuming the source point and the receiver point are not equal, \(z_s \neq z_r\), we must now solve a 2-point boundary-value problem. For convex interfaces (with both the source and the receiver located in the liquid) it is clear that direct (non refracted) or doubly transmitted rays can reach the receiver, Fig. 4.3(a). To calculate the path of the later, suppose the rays leave the source point \((x_s, z_s)\), intersect the interface at \((x_1, z_1)\), suffer refraction, intersect the interface again at \((x_2, z_2)\), suffer refraction again, and then reach the receiver point \((x_r, z_r)\). The shooting method obtains the ray path that connects the source point \((x_s,
and the receiver point \((x_r, z_r)\). We assume that the doubly transmitted ray intersects the vertical line \(x = x_r\) at \(z_3\) where in general \(z_3 \neq z_r\). The correct ray path is obtained when \(|z_3 - z_r|\) is less than a prescribed allowable tolerance \(\delta\). The ray path is then defined by \((x_s, z_s), (x_1, z_1), (x_2, z_2),\) and \((x_r, z_r)\). Now it is obvious that when the source is located in the liquid and the receiver is located in the solid, only singly transmitted rays may reach the receiver. Fig. 4.3(b). This ray path can be found in the same manner and is defined by \((x_s, z_s), (x_1, z_1)\) and \((x_r, z_3)\).

**Figure 4.3** Ray tracing \((z_s > 0)\) on a diametral plane for a convex solid-liquid interface showing (a) doubly transmitted rays and (b) singly transmitted rays.
Numerically simulated ray paths and wavefronts on the diametral plane for convex interfaces $h = 2, 5$ and $10$ mm are shown in Fig. 4.4(a) - (d), Fig. 4.5(a) - (d) and Fig. 4.6(a) - (d), respectively for source points located in the liquid ($z_s = 5, 10, 15$ and $20$ mm). When the source point is located in the liquid, ray paths in the liquid are straight whereas they are bent by the interface during propagation into the solid. Note that some of the rays are refracted at the first liquid-solid interface travel through the solid and are refracted again at the second solid-liquid interface (doubly transmitted rays) while others are only refracted once at the first liquid-solid interface (singly transmitted ray). In this case, doubly transmitted rays and rays with straight paths may both reach the same boundary point. However, these two kinds of rays are experimentally distinguishable because the doubly transmitted rays suffer energy losses due to reflection and mode conversion each time they cross the solid-liquid interface.

Wavefronts separate ultrasonically disturbed regions from those that are undisturbed. The TOF of an ultrasonic signal can in principle be measured at any receiver point on the diametral plane periphery that is intersected by a wavefront. The wavefronts at any time after source excitation can be obtained by connecting points along the collective set of ray paths with the same travel time. On the diametral plane the calculated quasi-longitudinal wavefronts for convex interface’s with source excitation points located in the liquid at $10$ $\mu$s intervals are also shown in Fig. 4.4 - 4.6. It is clear from Fig. 4.4 - 4.6, that as the source point is translated further away from the solid-liquid interface or as the interface height is decreased, the quasi-longitudinal wavefronts take a longer time to reach the receiver side of the ampoule due to the fact that a larger fraction of the total ray path is occupied by the slower velocity liquid.
Figure 4.4  Ray paths and wavefronts on a diametral plane for a convex interface with an interface height $h = 2$ mm for a source located in the liquid at (a) $z_s = 5$ mm, (b) $z_s = 10$ mm, (c) $z_s = 15$ mm and (d) $z_s = 20$ mm.
Figure 4.5 Ray paths and wavefronts on a diametral plane for a convex interface with an interface height $h = 5$ mm for a source located in the liquid at (a) $z_s = 5$ mm, (b) $z_s = 10$ mm, (c) $z_s = 15$ mm and (d) $z_s = 20$ mm.
Figure 4.6 Ray paths and wavefronts on a diametral plane for a convex interface with an interface height $h = 10$ mm for a source located in the liquid at (a) $z_s = 5$ mm, (b) $z_s = 10$ mm, (c) $z_s = 15$ mm and (d) $z_s = 20$ mm.
4.3.2 Source located in the solid \((z_s < 0)\)

Now suppose the source point is located in the solid \((z_s < 0)\). The interface and ray path (with initial ray angle \(\alpha\)) are still represented by Eqns. (4.3) and (4.4), respectively. For \(z_s < 0\) and an initial ray angle of \(\alpha < \alpha_c\), all the rays propagate in the solid along straight ray paths, where \(\alpha_c = \text{atan}(-z_s/2R_s) + \pi/2\) is the critical angle at which the ray path intersects the interface at \((x_0, z_0)\) where \(x_0 = R_s\) and \(z_0 = 0\). When \(\alpha > \alpha_c\), rays intersect the solid-liquid interface at \((x_1, z_1)\). Since the intersection point \((x_1, z_1)\) satisfies both Eqns. (4.3) and (4.4), it is obtained as one of two roots. Since the intersection point is greater than the critical point \((x_0, z_0)\), the root with \(z_1 > z_0\) was chosen.

Again, the ray’s incident angle to the interface, \(\theta_{sol}\), is defined as the angle between the normal to the interface at \((x_1, z_1)\) and the ray path given by Eqn. (4.4). The equation for the normal to the interface at \((x_1, z_1)\) was previously given by Eqn. (4.8). The incident ray angle \(\theta_{sol}\) is

\[
\theta_{sol} = \cos \left[ \frac{c^2 - a^2 - b^2}{-2ab} \right]
\]

(4.14)

where:

\[
a = \sqrt{(x_1 - x_s)^2 + (z_1 - z_s)^2}
\]

\[
b = \sqrt{x_1^2 + [z_1 + (R_c - |h|)]^2}
\]

\[
c = \sqrt{x_s^2 + [z_s + (R_c - |h|)]^2}
\]

The refraction angle, \(\theta_{liq}\), at \((x_1, z_1)\) can be calculated next. Again, the refraction angle \(\theta_{liq}\) of the refracted ray in the liquid can be determined using Snell’s law:

\[
\theta_{liq} = \sin \left[ \frac{v_{liq}}{v_{sol}} \sin \theta_{sol} \right].
\]

(4.15)
Therefore, this single transmitted ray path is defined by the source point \((x_s, z_s)\), the solid-liquid interface intersection \((x_1, z_1)\) and the refraction angle \(\theta_{\text{liq}}\). The procedure for determining the ray paths and TOF's is similar to that previously outlined. When the source is located in the solid \((z_s < 0)\) and the receiver is located in the liquid \((z_r > 0)\), it is clear that only singly transmitted rays are permissible, Fig. 4.7(a). In the case where both the source and the receiver are located in the solid, only non refracted (direct) rays propagate from the source to the receiver, Fig. 4.7(b).

Figure 4.7 Ray tracing \((z_s < 0)\) on a diametral plane for a convex solid-liquid interface showing (a) singly transmitted rays and (b) non refracted rays.
Numerically simulated ray paths and wavefronts on the diametral plane for convex interfaces $h = 2, 5$ and $10$ mm are shown in Fig. 4.8(a) - (d), Fig. 4.9(a) - (d) and Fig. 4.10(a) - (d), respectively for source points located in the solid ($z_s = -5, -10, -15$ and $-20$ mm). When the source point is located in the solid, ray paths in the solid are straight whereas they are bent by the interface during propagation into the liquid. Unlike the previous sensing configuration, ray paths for this configuration are only refracted once at the liquid-solid interface (singly transmitted ray).

The calculated quasi-longitudinal wavefronts for convex interface’s with source excitation points located in the liquid at $10 \mu s$ intervals are also shown in Fig. 4.8 - 4.10. Again, it is clear from Fig. 4.8 - 4.10, that as the source point is translated further away from the solid-liquid interface or as the interface height is decreased, the quasi-longitudinal wavefronts take a longer time to reach the receiver side of the ampoule due to the fact that a larger fraction of the total ray path is occupied by the slower velocity liquid.
Figure 4.8 Ray paths and wavefronts on a diametral plane for a convex interface with an interface height $h = 2$ mm for a source located in the solid at (a) $z_s = -5$ mm, (b) $z_s = -10$ mm, (c) $z_s = -15$ mm and (d) $z_s = -20$ mm.
Figure 4.9 Ray paths and wavefronts on a diametral plane for a convex interface with an interface height $h = 5$ mm for a source located in the solid at (a) $z_s = -5$ mm, (b) $z_s = -10$ mm, (c) $z_s = -15$ mm and (d) $z_s = -20$ mm.
Figure 4.10 Ray paths and wavefronts on a diametral plane for a convex interface with an interface height $h = 10$ mm for a source located in the solid at (a) $z_s = -5$ mm, (b) $z_s = -10$ mm, (c) $z_s = -15$ mm and (d) $z_s = -20$ mm.
4.3.3 Discussion

The locality of the source excitation point (i.e. in either the liquid or solid phase) produces two uniquely different projections of ray paths and wavefronts. Direct or non refracted wavefronts may be produced for both sensing configurations when the source and receiver points are located in the same phase. However, these can be readily distinguished because of the velocity difference between the solid and liquid phases. Singly transmitted ray are produced for both sensing configurations when the source and receiver points are located in different phases (i.e. \( z_s > 0 \) and \( z_r < 0 \) or \( z_s < 0 \) and \( z_r > 0 \)). Doubly transmitted rays are produced for convex interfaces only when both the source and receiver points are located in the liquid phase (i.e. \( z_s > 0 \) and \( z_r > 0 \)).

The relative locality of the source point with respect to the interface position (\( z_i = 0 \)) produces a shift of the wavefront projections. For a source point located in the liquid and a translation of the source point further away from the solid-liquid interface or a source point located in the solid and a translation of the source point away from the solid-liquid interface, the time needed for the quasi-longitudinal wavefronts to reach the receiver side of the ampoule increases due to the longer total ray path. This effect is more pronounced for projections with the source located in the slower velocity liquid.

The interfacial height (\( h \)) also produces a shift of the wavefront projections. Whether the source point is located in either the liquid or the solid, as the interface height is decreased, the quasi-longitudinal wavefronts take a longer time to reach the receiver side of the ampoule. Again this is due to the fact that a larger fraction of the total ray path is occupied by the slower velocity liquid. In addition, this effect is more pronounced for doubly transmitted rays when the source is located in the liquid, because the fraction of total ray path length in the slower velocity liquid is larger in the doubly transmitted rays as compared with singly transmitted rays.
4.4 Concave Interfaces ($h < 0$)

4.4.1 Source located in the liquid ($z_s > 0$)

Now consider a concave interface shape, and ray paths for prescribed source ($x_s$, $z_s$) coordinates with initial ray angles $\alpha$. On the diametral plane, the interface is defined by the equation for a circle of radius $R_c$:

$$R_c^2 = x^2 + [z - (R_c - |h|)]^2. \tag{4.16}$$

The equation for a ray path (with initial ray angle $\alpha$) is

$$x = \tan \alpha (z - z_s) + x_s. \tag{4.17}$$

Suppose a source point is located in the liquid ($z_s > 0$). The interface and ray path (with initial ray angle $\alpha$) are represented by Eqns. (4.16) and (4.17), respectively. For $z_s > 0$ and an initial ray angle of $\alpha > \alpha_c$ all the rays propagate in the liquid along straight ray paths, where $\alpha_c = \frac{\tan^{-1}(-z_s/2R_s)}{\pi/2}$ is the critical angle at which the ray path intersects the interface at $(x_0, z_0)$ where $x_0 = R_s$ and $z_0 = 0$. When $\alpha < \alpha_c$, rays intersect the solid-liquid interface at $(x_1, z_1)$. Since the intersection point $(x_1, z_1)$ satisfies both Eqns. (4.16) and (4.17), it is obtained as one of two roots. Since the intersection point is less than the critical point $(x_0, z_0)$, the root with $z_1 < z_0$ was chosen.

Again, the ray's incident angle to the interface, $\theta_{i,\text{liq}}$, is defined as the angle between the normal to the interface at $(x_1, z_1)$ and the ray path given by Eqn. (4.17). The equation for the normal to the interface at $(x_1, z_1)$ can be written

$$x[z_1 - (R_c - |h|)] - x_1 z = 0. \tag{4.18}$$
The incident ray angle $\theta_{\text{liq}}$ is

$$
\theta_{\text{liq}} = \arccos\left[\frac{c^2 - a^2 - b^2}{-2ab}\right] \tag{4.19}
$$

$$
a = \sqrt{(x_1 - x_s)^2 + (z_1 - z_s)^2}
$$

$$
b = \sqrt{x_1^2 + [z_1 - (R_c - |h|)]^2}
$$

$$
c = \sqrt{x_s^2 + [z_s - (R_c - |h|)]^2}
$$

The refraction angle, $\theta_{\text{sol}}$, at $(x_1, z_1)$ can be calculated next. Again, the refraction angle $\theta_{\text{sol}}$ of the refracted ray in the liquid can be determined using Snell's law:

$$
\theta_{\text{sol}} = \arcsin\left[\frac{v_{\text{sol}}}{v_{\text{liq}}}\sin\theta_{\text{liq}}\right]. \tag{4.20}
$$

Therefore, this single transmitted ray path is defined by the source point $(x_s, z_s)$, the solid-liquid interface intersection $(x_1, z_1)$ and the refraction angle $\theta_{\text{sol}}$. The procedure for determining the ray paths and TOF’s is similar to that previously outlined. When the source is located in the liquid ($z_s > 0$) and the receiver is located in the solid ($z_r < 0$), it is clear that only singly transmitted rays are permissible, Fig. 4.11(a). In the case where both the source and the receiver are located in the liquid, only non refracted (direct) rays propagate from the source to the receiver, Fig. 4.11(b).
Figure 4.11 Ray tracing \( z_s > 0 \) on a diametral plane for a concave solid-liquid interface showing (a) singly transmitted rays and (b) non refracted rays.

Numerically simulated ray paths and wavefronts on the diametral plane for concave interfaces \( h = -2, -5 \) and \(-10 \) mm are shown in Fig. 4.12(a) - (d), Fig. 4.13(a) - (d) and Fig. 4.14(a) - (d), respectively for source points located in the liquid \( (z_s = 5, 10, 15 \) and \( 20 \) mm). When the source point was located in the liquid, ray paths in the liquid were straight whereas they are bent by the interface during propagation into the solid. It is interesting to note that none of the rays are doubly transmitted, they can only be refracted once at the liquid-solid interface (singly transmitted rays). However, due to the divergent nature of the concave interface, there may be a region of non propagation \( (i.e. \) dark zone) in the solid in which the wavefront does not intersect the outer boundary. The first dark zone on the left \( (x < 0) \) is due to ray bending caused by the curvature of the interface; while no rays travel
through the second dark zone \((x > 0)\) because the refraction angle in the solid is greater than \(\pi/2\).

The magnitude of the first dark zone is solely a function of the interfacial height; that is as the interface height becomes increasingly negative, the magnitude of the dark zone increases. It is also interesting to note that the magnitude of the second dark zone increases in size as the convexity of the interface becomes increasingly negative and decreases in size as the source point is translated away from the solid-liquid interface. It is clear from Fig. 4.12 - 4.14, that as the source point is translated further away from the solid-liquid interface the quasi-longitudinal wavefronts take a longer time to reach the receiver side of the ampoule due to the fact that a larger fraction of the total ray path is occupied by the slower velocity liquid.
Figure 4.12 Ray paths and wavefronts on a diametral plane for a concave interface with an interface height $h = -2\, \text{mm}$ for a source located in the liquid at (a) $z_s = 5\, \text{mm}$, (b) $z_s = 10\, \text{mm}$, (c) $z_s = 15\, \text{mm}$ and (d) $z_s = 20\, \text{mm}$. 
Figure 4.13 Ray paths and wavefronts on a diametral plane for a concave interface with an interface height $h = -5$ mm for a source located in the liquid at (a) $z_s = 5$ mm, (b) $z_s = 10$ mm, (c) $z_s = 15$ mm and (d) $z_s = 20$ mm.
Figure 4.14 Ray paths and wavefronts on a diametral plane for a concave interface with an interface height \( h = -10 \text{ mm} \) for a source located in the liquid at (a) \( z_s = 5 \text{ mm} \), (b) \( z_s = 10 \text{ mm} \), (c) \( z_s = 15 \text{ mm} \) and (d) \( z_s = 20 \text{ mm} \).
4.4.2 Source located in the solid ($z_s < 0$)

Now suppose the source point is located in the solid ($z_s < 0$). The interface and ray path (with initial ray angle $\alpha$) are still represented by Eqns. (4.16) and (4.17), respectively. For $z_s < 0$ and an initial ray angle of $\alpha < \alpha_c$ all the rays propagate in the solid along straight ray paths, where $\alpha_c = \tan(-z_s/2R_y) + \pi/2$ is the critical angle at which the ray path intersects the interface at $(x_0, z_0)$.

The equation for the ray path that intersects the circle tangentially at $(x_0, z_0)$ and propagates only in the liquid without suffering refraction is given by

$$x_0x + [z_0-(R_c-|h|)][z-(R_c-|h|)] = R_c^2,$$  \hspace{1cm} (4.21)

where the coordinates for the tangential point $(x_0, z_0)$ to the interface are given by

$$x_0 = \frac{R_c^2 - [z_0-(R_c-|h|)]z_s'}{x_s},$$  \hspace{1cm} (4.22)

$$z_0 = \frac{R_c^2z_s'}{x_s^2 + z_s'^2} + R_c \sqrt{\left(\frac{R_c z_s'}{x_s^2 + z_s'^2}\right)^2 - \frac{R_c^2}{x_s^2 + z_s'^2}} - \frac{R_c^2 - x_s^2}{x_s^2 + z_s'^2} + (R_c-|h|),$$  \hspace{1cm} (4.23)

where $z_s' = z_s - (R_c-|h|)$.

When $\alpha > \alpha_c$, rays intersect the liquid-solid interface at $(x_1, z_1)$. Since the intersection point $(x_1, z_1)$ satisfies both Eqns. (4.16) and (4.17), it is obtained as one of two roots. Since the intersection point is to the left side of the tangential point $(x_0, z_0)$, the root with $x_1 < x_0$ was chosen. Again, the ray's incident angle to the interface, $\theta_{\text{sol}}$, is defined as the angle between the normal to the interface at $(x_1, z_1)$ and the ray path given by Eqn. (4.17). The equation for the normal to the interface at $(x_1, z_1)$ is given by Eqn. (4.18). The rays
incident angle with the solid-liquid interface $\theta_{sol}$ and the refraction angle $\theta_{liq}$ can be found from Eqns. (4.19) and (4.20).

Therefore, this single transmitted ray path is defined by the source point $(x_s, z_s)$, the solid-liquid interface intersection $(x_1, z_1)$ and the refraction angle $\theta_{liq}$. The procedure for determining the ray paths and TOF’s is similar to that previously outlined. When the source is located in the solid $(z_s < 0)$ and the receiver is located in the liquid $(z_r > 0)$, it is clear that only singly transmitted rays are permissible, Fig. 4.15(a). In the case where both the source and the receiver are located in the solid, only non refracted (direct) rays propagate from the source to the receiver, Fig. 4.15(b).

![Ray tracing](image)

**Figure 4.15** Ray tracing $(z_s < 0)$ on a diametral plane for a concave solid-liquid interface showing (a) singly transmitted rays and (b) non refracted rays.
Numerically simulated ray paths and wavefronts on the diametral plane for concave interfaces $h = -2, -5$ and $-10$ mm are shown in Fig. 4.16(a) - (d), Fig. 4.17(a) - (d) and Fig. 4.18(a) - (d), respectively for source points located in the solid ($z_r = -5.10.15$ and $-20$ mm). When the source point was located in the solid, ray paths in the solid were straight whereas they are bent by the interface during propagation into the liquid. Again, due to the divergent nature of the concave interface, there may be a region of non propagation (i.e. dark zones) in the liquid in which the wavefront does not intersect the outer boundary. The first dark zone on the left ($x < 0$) is due to ray bending caused by the curvature of the interface; while no rays travel through the second dark zone ($x > 0$) because the refraction angle in the solid is greater than $\pi/2$.

The magnitude of the first dark zone is solely a function of the interfacial height; that is as the interface height becomes increasingly negative, the magnitude of the dark zone increases. It is also interesting to note that the magnitude of the second dark zone increases in size as the convexity of the interface becomes increasingly negative and decreases in size as the source point is translated away from the solid-liquid interface. Again, it is clear from Fig. 4.16 - 4.18, that as the source point is translated further away from the solid-liquid interface the quasi-longitudinal wavefronts take a longer time to reach the receiver side of the ampoule due to the fact that a larger fraction of the total ray path is occupied by the faster velocity solid. However, the effect is more pronounced for concave interfaces when the source point was located in the slower velocity liquid.
Figure 4.16 Ray paths and wavefronts on a diametral plane for a concave interface with an interface height $h = -2$ mm for a source located in the solid at (a) $z_s = -5$ mm, (b) $z_s = -10$ mm, (c) $z_s = -15$ mm and (d) $z_s = -20$ mm.
Figure 4.17 Ray paths and wavefronts on a diametral plane for a concave interface with an interface height $h = -5$ mm for a source located in the solid at (a) $z_s = -5$ mm, (b) $z_s = -10$ mm, (c) $z_s = -15$ mm and (d) $z_s = -20$ mm.
Figure 4.18 Ray paths and wavefronts on a diametral plane for a concave interface with an interface height \( h = -10 \) mm for a source located in the solid at (a) \( z_s = -5 \) mm, (b) \( z_s = -10 \) mm, (c) \( z_s = -15 \) mm and (d) \( z_s = -20 \) mm.
4.4.3 Discussion

The locality of the source excitation point (i.e. in either the liquid or solid phase) produces two uniquely different projections of ray paths and wavefronts. Direct or non-refracted wavefronts are produced for both sensing configurations when the source and receiver points are located in the same phase. However, these can be readily distinguished because of the velocity difference between the solid and liquid phases. Singly transmitted ray are produced for both sensing configurations when the source and receiver points are located in different phases (i.e. \( z_s > 0 \) and \( z_r < 0 \) or \( z_s < 0 \) and \( z_r > 0 \)). No doubly transmitted rays are produced these sensing configuration with concave interfaces.

The relative locality of the source point with respect to the interface position (\( z_i = 0 \)) produces a shift of the wavefront projections. For a source point located in the liquid and translation of the source point further away from the solid-liquid interface or a source point located in the solid and translation of the source point away from the solid-liquid interface the time needed for the quasi-longitudinal wavefronts to reach the receiver side of the ampoule increases due to longer total ray path. This effect is more pronounced for projections with the source located in the slower velocity liquid.

The interfacial height (\( h \)) also produces a shift of the wavefront projections. Whether the source point is located in either the liquid or the solid, as the interfacial height is decreased, the quasi-longitudinal wavefronts take a longer time to reach the receiver side of the ampoule. Again this is due to the fact that a larger fraction of the total ray path is occupied by the slower velocity liquid and this effect is more pronounced for projections with the source located in the slower velocity liquid.
4.5 Planar Interface \((h = 0)\)

The procedure for determining the ray paths and wavefronts for a planar interface are similar in nature to both the convex and concave interfaces and therefore not shown here. Equations (4.4) and (4.17) may be solved for \(z = 0\) to find the point where the rays intersect the solid-liquid interface at \((x_1, z_1)\). The incident and refracted angles are also computed in the same manner as before.

Numerically simulated ray paths and wavefronts on the diametral plane for a planar interface \((h = 0 \text{ mm})\) are shown in Fig. 4.19(a) - (d) for source points located in the liquid \((z_s = 5, 10, 15 \text{ and } 20 \text{ mm})\), where Fig. 4.20(a) - (d) shows the ray paths and wavefronts for source points located in the solid \((z_s = -5, -10, -15 \text{ and } -20 \text{ mm})\). It should be noted that a planar interface is a degenerate case between the convex and concave interfacial curvatures. Therefore it is expected that there would be no dark zones or doubly transmitted rays. Therefore when the source point is located in the liquid, ray paths in the liquid are straight and when the source point is located in the solid, ray paths in the solid are straight. In both cases, when the source and receiver points are located in different phases \(i.e. z_s > 0 \text{ and } z_r < 0 \text{ or } z_s < 0 \text{ and } z_r > 0\) ray paths for this configuration are only refracted once at the liquid-solid interface (singly transmitted ray).

The calculated quasi-longitudinal wavefronts for a planar interface with source excitation points located in the liquid and solid at 10 \(\mu\)s intervals are also shown in Fig. 4.19 and Fig. 4.20, respectively. Again, it is clear from Fig. 4.19 and 4.20, that as the source point is translated further away from the solid-liquid interface, the quasi-longitudinal wavefronts take a longer time to reach the receiver side of the ampoule. This effect is more pronounced for projections with the source located in the slower velocity liquid.
Figure 4.19 Ray paths and wavefronts on a diametral plane for a planar interface \( h = 0 \text{ mm} \) for a source located in the liquid at (a) \( z_s = 5 \text{ mm} \), (b) \( z_s = 10 \text{ mm} \), (c) \( z_s = 15 \text{ mm} \) and (d) \( z_s = 20 \text{ mm} \).
Figure 4.20 Ray paths and wavefronts on a diametral plane for a planar interface ($h = 0$ mm) for a source located in the solid at (a) $z_s = -5$ mm, (b) $z_s = -10$ mm, (c) $z_s = -15$ mm and (d) $z_s = -20$ mm.
4.6 Summary

A detailed two-dimensional ray path and wavefront analysis has been conducted on the diametral plane of model (convex, planar and concave) isotropic solid-liquid interfaces. These simulations indicate that the solid:liquid velocity ratio and the curvature of the interface together control ray bending behavior. It has also been determined that the convex, planar and concave interfaces produce uniquely different wavefront projections and the wavefront projections are also affected by the location of the source excitation point with respect to the liquid-solid interface. These results indicate that using these sensing configurations should lead to unique time of flight projection data sets for determining the location and convexity of the liquid-solid interface using transmission TOF projections. In addition the severe nature of the ray bending requires precise knowledge of ray paths in order to use TOF data for interface reconstruction. The following chapter will address the experimental validation of the ray path and wavefront analysis.
Chapter 5

Experimental Evaluation of Diametral Sensing

The sensing methodology outlined in the previous chapter indicated that transmission TOF data taken in the diametral plane leads to unique solutions for a variety of interfacial convexities and source/receiver sensing configurations. This chapter seeks to validate those models by analyzing the boundary value problem for the TOF projections and assessing their validity using laser ultrasonically generated and detected ultrasound taken in the diametral plane of these simulated interfaces.

5.1 Experimental Geometry

The bench-top model with known, solid-liquid velocities, consisted of water and solid polymethylmethacrylate (PMMA) contained in a cylindrical aluminum (2024-T6) “ampoule”. To maintain good ultrasonic coupling, the solid PMMA was machined such that the diameter was slightly smaller (0.50 mm) than the inner diameter of the aluminum ampoule to allow a thin layer of liquid (0.25 mm) to exist between the inner wall of the ampoule and solid PMMA. By machining the end of the PMMA, the interface curvature was varied from convex to planar to concave (viewed toward the liquid). The interface
convexities \( h \) (defined such that \( h > 0 \) corresponds to a convex interface and \( h < 0 \) a concave interface) studied were \( h = \pm 2, \pm 5, \pm 10 \text{ mm} \) and planar (\( h = 0 \text{ mm} \)). The aluminum ampoule had an inner radius of \( 75.0 \pm 0.1 \text{ mm} \) and an outer radius of \( 77.0 \pm 0.1 \text{ mm} \). The water and PMMA had a measured longitudinal wave velocity of \( 1.50 \pm 0.01 \text{ mm/\mu s} \) and \( 2.67 \pm 0.01 \text{ mm/\mu s} \) at \( 21^\circ \text{C} \), respectively. The 6061-T6 Al alloy had a measured longitudinal wave velocity of \( 6.35 \pm 0.01 \text{ mm/\mu s} \) and a shear wave velocity of \( 3.01 \pm 0.01 \text{ mm/\mu s} \) at \( 21^\circ \text{C} \).

### 5.2 Making Measurements

Ultrasonic time-of-flights (TOF's) between precisely positioned source and receiver points were measured using the laser ultrasonic system shown in Fig. 5.1. A \(~10 \text{ ns} \) duration \( Q \)-switched Nd:YAG (Coherent) laser pulse of \( 1.064 \mu \text{m} \) wavelength was used as the ultrasonic source. The energy per pulse was \(~15 \text{ mJ} \). The roughly Gaussian beam of the multimode pulse was focused to an approximate circular spot \( 0.5 \text{ mm} \) in diameter. Thus, the source power density was \(~1500 \text{ MW/cm}^2 \). The low infrared absorption coefficient for the aluminum required the use of a constraining layer consisting of a glass slide and a propylene glycol couplant. The ultrasonic receiver was a heterodyne laser interferometer (Ultra Optek OP-35-O), which responded to the sample's out-of-plane (normal) surface displacement associated with wavefront arrivals at the receiver point. It was powered by a \( 5 \text{ mW} \) single mode HeNe laser, which produced a continuous Gaussian beam of \( 514 \text{ nm} \) wavelength focused to a circular spot on the sample \(~100 \mu \text{m} \) in diameter.

The output signal from the interferometer was bandpass filtered between \( 10 \text{ kHz} \) and \( 10 \text{ MHz} \) and recorded with a precision digital oscilloscope (LeCroy 7200) at a \( 2 \text{ ns} \) sampling interval using 8-bit analog-to-digital conversion. To improve the signal to noise ratio, each waveform used for a TOF measurement was the average of \(~25 \) pulses col-
lected at a pulse repetition rate of 20 Hz. A fast photodiode identified the origination time for the ultrasonic signals.

Two sets of computer controlled translation stages were positioned such that the ampoule could be translated along the z-axis allowing the fixed receiver’s position to be located at any point on the diametral plane (i.e. in the solid or liquid phase) and the source could be independently translated to acquire a fan-beam ultrasonic TOF projection data set. This arrangement was chosen because axial translation of the source was experimentally easier than axial translation of the receiver. Multiple ultrasonic TOF projection scans were acquired for each interface in two sensing configurations. The first configuration positioned the receiver in the liquid ($z_r = 5, 10, 15, \text{ and } 20$ mm) and the second in the solid phase ($z_r = -5, -10, -15, \text{ and } -20$ mm) relative to the interface edge. The source was axially scanned from the liquid phase ($z_s = 40$ mm) to the solid phase ($z_s = -20$ mm) at 1 mm increments for each TOF projection set. The translational stages position accuracy was 1.175 μm per 5.08 mm of linear motion. Errors in measured sample sizes, imprecision in the translation stage alignment, temperature fluctuations, etc., resulted in an estimated TOF error of about ±100 ns.
Figure 5.1 A schematic of the laser ultrasonic test facility used to evaluate sensor concepts.
The output from the laser ultrasonic sensor's interferometer is in the form of a surface displacement versus time-of-flight waveform. Each waveform is stored as an individual trace and therefore can be analyzed discretely. The simplest method to determine the arrival time-of-flight's is to digitally pick-off each arrival time. This was accomplished by using the LeCroy digital oscilloscope. The arrival time-of-flight was chosen as the time at which the interferometer displacement was twice that of the RMS noise level of the digital waveform. This was chosen because of its convenience, accuracy and repeatability in time-of-flight measurement.

5.3 Convex Interfaces (h > 0)

5.3.1 Receiver above interface (z, > 0)

Two typical ultrasonic waveforms for a convex interface (h = 5 mm) are shown in Fig. 5.2(a) and Fig. 5.2(b). Figure 5.2(a) and Fig. 5.2(b) show two distinct sensor arrangements; Fig. 5.2(a) where the source is located in the liquid phase (z, = 16 mm) and Fig. 5.2(b) where the source is located in the solid phase (z, = -11 mm) for a receiver that is located in the liquid phase (z, = 15 mm). Both show two oscilloscope traces; one common to both which is the photodiode pulse denoting the start time for the ultrasonic wavefront and the second is the surface displacement recorded by the interferometer. Both figures display minor arrival events at ~22 μs which correspond to the arrival of an encircling wave in the ampoule. In Fig. 5.2(a) two major arrival events were observed, the first event is due to the arrival of a doubly transmitted ray (TOF = 42.92 μs) and the second of a (straight) non refracted ray (TOF = 50.67 μs). In Fig. 5.2(b) only one major arrival was observed, due to the arrival of a singly transmitted ray (TOF = 36.27 μs).
Figure 5.2 Typical ultrasonic waveforms denoting the arrival time-of-flights (TOF’s) where the source is located in (a) the liquid ($z_s = 16$ mm) and (b) the solid ($z_s = -11$ mm) for a receiver located in the liquid phase ($z_r = 15$ mm).
Because the geometry of the model solid-liquid interface system is known in addition to the source and receiver points, the theoretical time of flight for the potential ray paths can be determined. Table 5.1 shows the mathematical representation of the possible ray paths encountered for convex interfaces \((h > 0)\) with the receiver located in the liquid \((z_r < 0)\). The TOF of each type of ray path were computed as a function of both the source \((x_s, z_s)\) and the receiver \((z_r, z_r)\) points and compared with the experimental data.

<table>
<thead>
<tr>
<th>Table 5.1: Possible ray paths encountered for convex interfaces ((h &gt; 0)) with the receiver located in the liquid ((z_r &gt; 0)).</th>
</tr>
</thead>
<tbody>
<tr>
<td>non refracted (\tau_{nr} = \sqrt{\frac{(x_r-x_s)^2 + (z_r-z_s)^2}{v_{\text{liquid}}}} ) ((5.1))</td>
</tr>
<tr>
<td>doubly transmitted (\tau_{dt} = \sqrt{\frac{(x_1-x_s)^2 + (z_1-z_s)^2}{v_{\text{liquid}}}} + \sqrt{\frac{(x_2-x_1)^2 + (z_2-z_1)^2}{v_{\text{solid}}}} ) ((5.2))</td>
</tr>
<tr>
<td>(\quad + \sqrt{\frac{(x_r-x_2)^2 + (z_r-z_2)^2}{v_{\text{liquid}}}} )</td>
</tr>
<tr>
<td>singly transmitted (\tau_{st} = \sqrt{\frac{(x_1-x_s)^2 + (z_1-z_s)^2}{v_{\text{solid}}}} + \sqrt{\frac{(x_r-x_1)^2 + (z_r-z_1)^2}{v_{\text{liquid}}}} ) ((5.3))</td>
</tr>
</tbody>
</table>

1. Cartesian coordinate system in mm. \(v_l\) = liquid velocity \((\text{mm/}\mu\text{s})\), \(v_s\) = solid velocity \((\text{mm/}\mu\text{s})\).
The most convenient manner to present the time-of-flight data is in the form of fan-beam ultrasonic TOF projections. Since, in this model system both the location of the interface \((z_i)\) and the receiver \((z_r)\) are known, the TOF projections can be viewed several different ways. The first manner normalizes the interface position \((z_i = 0)\), which allows the receiver position \((z_r)\) to be transitory and the second normalizes the receiver position \((z_r = 0)\), which allows the interface position \((z_i)\) to be transitory.

The TOF projection data of convex interfaces \((h = 2, 5, 10 \text{ and } 10 \text{ mm})\) for a constant interface position \((z_i = 0)\) are shown in Figs. 5.3(a) - (d) for a receiver located in the liquid at locations \(z_r = 5, 10, 15 \text{ and } 20 \text{ mm}\), respectively. In Fig. 5.3 the TOF of rays generated in the solid \((z_s < 0)\) corresponds to singly transmitted rays. When the source is located in the liquid \((z_s > 0)\) two TOF arrivals corresponding to the doubly transmitted and direct rays are shown. The TOF projection data of Fig. 5.3 shows good agreement between the experimentally determined TOF's and the numerically simulated data predicted by the ray path model.

From direct observation of the TOF projection data, Fig. 5.3, the interface location \((z_i)\) is easily identified by the transition of direct and doubly transmitted rays to singly transmitted rays at the interface edge \((z_i = 0)\). Also, the TOF of doubly transmitted rays coincides with that of the singly transmitted rays at \(z_i = 0\) for each interface convexity, which is the minimum in the projection data. The TOF profiles of direct rays in the liquid are constant for all interface convexities. However, the TOF data profiles of singly and doubly transmitted rays are shifted to the left \((i.e. \text{ slower TOF's})\) as the interface convexity \(h\) is increased. This is intuitive; as the convexity is increased the fraction of the total path length of the ray in the lower velocity liquid decreases and the fraction in the higher velocity solid increases resulting in an overall decrease in TOF. Also, it is interesting to note that as the receiver's position is translated further from the interface edge \((z_r = 5, 10, 15\)
and 20 mm) the overall TOF project for each interface convexity shifts to increased TOF values and the relative time spacing between the interfaces (h = 2, 5 and 10 mm) also increases.

The TOF projection data for convex interfaces versus a constant receiver position \( z_r = 0 \) for interfacial heights of 2, 5 and 10 mm are shown in Fig. 5.4(a) - (c), respectively. In Fig. 5.4 the TOF of rays generated in the solid \( z_s < z_i \) correspond to singly transmitted rays. When the source is located in the liquid \( z_s > z_i \) two TOF arrivals corresponding to the doubly transmitted and direct rays are shown. Again, the TOF projection data of Fig. 5.4 shows good agreement between the experimentally determined TOF's and the numerically simulated data predicted by the ray path model.

Now, it should be noted that comparison of Fig. 5.3 and Fig. 5.4 provides a clear insight to the effects of both interfacial height and position, with respect to the known receiver's position. It is clear from Fig. 5.3 that when the position of the interface edge is normalized \( z_i = 0 \), the difference in interfacial height \( h \) can be readily observed for the three interfaces examined here. It should be also noted from Fig. 5.4 that when the receiver's position is normalized \( z_r = 0 \), the relative position of the interface's edge \( z_i \) is readily observed. Therefore, by displaying the TOF projection data in two different manners, both the interfacial height \( h \) and the position \( z_i \) can be readily distinguished for convex interface shapes when the receiver's position is located in the liquid.
Figure 5.3 Ultrasonic time-of-flight projection data of convex interfaces, \( h = 2, 5, \) and 10 mm, for a fixed interface position \( (z_i = 0) \) with the receiver located in the liquid at (a) \( z_r = 5 \) mm, (b) \( z_r = 10 \) mm, (c) \( z_r = 15 \) mm and (d) \( z_r = 20 \) mm.
Figure 5.4 Ultrasonic time-of-flight projection data for convex interfaces versus a constant receiver position ($z_r = 0$) for interfacial heights of (a) $h = 2$ mm, (b) $h = 5$ mm, and (c) $h = 10$ mm.
5.3.2 Receiver below interface \((z_r < 0)\)

Two typical ultrasonic waveforms for a convex interface \((h = 5 \text{ mm})\) are shown in Fig. 5.5(a) and (b). Figure 5.5(a) and (b) show two distinct sensor arrangements: Fig. 5.5(a) where the source is located in the liquid phase \((z_s = 15 \text{ mm})\) and Fig. 5.5(b) where the source is located in the solid phase \((z_s = -13 \text{ mm})\) for a receiver that is located in the solid phase \((z_r = -15 \text{ mm})\). Both show two oscilloscope traces; one common to both which is the photodiode pulse denoting the start time for the ultrasonic wavefront and the second is the surface displacement recorded by the interferometer. Both figures display minor arrival events at \(-22 \mu s\) which correspond to the arrival of an encircling wave in the ampoule. In Fig. 5.5(a) one major arrival event was observed, this event is due to the arrival of a singly transmitted ray (TOF = 35.11 \mu s). In Fig. 5.5(b) another major arrival was observed, due to the arrival of a non refracted ray (TOF = 28.35 \mu s).

Table 5.2 shows the mathematical representation of the possible ray paths encountered for convex interfaces \((h > 0)\) with the receiver located in the solid \((z_r < 0)\). The TOF of each type of ray path was computed as a function of both the source \((x_s, z_s)\) and the receiver \((z_r, z_r)\) points and compared with the experimental data. Again the projection data can be plotted by normalizing the interface position \((z_i = 0)\), which allows the receiver position \((z_r)\) to be transitory and normalizing the receiver position \((z_r = 0)\), which allows the interface position \((z_i)\) to be transitory. The ultrasonic TOF projection data for convex interfaces \((h = 2, 5 \text{ and } 10 \text{ mm})\) is shown in Fig. 5.6(a) - (d) for a receiver located in the solid \((z_r = -5, -10, -15 \text{ and } -20 \text{ mm})\), respectively. In Fig. 5.6 the TOF of rays generated in the solid \((z_s < 0)\) corresponds to direct rays. When the source is located in the liquid \((z_s > 0)\) only singly transmitted rays were observed. Again the TOF projection data shows good agreement between the experimentally determined TOF's and the numerically simulated data predicted by the model.
Figure 5.5 Typical ultrasonic waveforms denoting the arrival time-of-flights (TOF's) where the source is located in (a) the liquid ($z_s = 15$ mm) and (b) the solid ($z_s = -13$ mm) for a receiver located in the liquid phase ($z_r = -15$ mm).
Table 5.2: Possible ray paths encountered for convex interfaces \((h > 0)\) with the receiver located in the solid \((z_r < 0)\).

\[
\tau_{st} = \sqrt{\frac{(x_1 - x_s)^2 + (z_1 - z_s)^2}{v_{\text{liquid}}} + \frac{(x_r - x_1)^2 + (z_r - z_1)^2}{v_{\text{solid}}}} \quad (5.4)
\]

\[
\tau_{nr} = \sqrt{\frac{(x_r - x_s)^2 + (z_r - z_s)^2}{v_{\text{solid}}}} \quad (5.5)
\]

When the receiver is located in the solid the interface location is again easily identified by the transition of singly transmitted rays to direct rays at the interface edge \((z_i = 0)\). The TOF of singly transmitted ray paths coincides with that of direct ray paths at \(z_i = 0\) for all interface convexities. The TOF of direct rays in the solid is constant for all interface convexities at each receiver location. However, the TOF of direct rays has a minimum at \(z_r\) due to a minimum in the ray path length. Similar to before, the TOF data projections of singly transmitted rays are shifted to slower TOF’s as the interface convexity is increased. Again, this is intuitive; as the convexity increases the ray travels more in the solid and less in the liquid resulting in slower TOF’s. Again, it is interesting to note that as the receiver’s position is translated further from the interface edge \((z_r = -5, -10, -15\) and \(-20 \text{ mm}\)) the overall TOF project for each interface convexity shifts to increased TOF values. However this affect is not as pronounced with the receiver located in the solid.

1. Cartesian coordinate system in mm. \(v_{\text{liquid}} = \text{ liquid velocity (mm/\mu s)}\), \(v_{\text{solid}} = \text{ solid velocity (mm/\mu s)}\).
The TOF projection data for convex interfaces versus a constant receiver position \( z_r = 0 \) for interfacial heights of 2, 5 and 10 mm is shown in Fig. 5.7(a) - (c), respectively. In Fig. 5.7 the TOF of rays generated in the solid \( z_s < z_l \) corresponds to direct rays. When the source is located in the liquid \( z_s > z_l \) only singly transmitted rays are shown. Again, the TOF projection data of Fig. 5.7 shows good agreement between the experimentally determined TOF's and the numerically simulated data predicted by the ray path model.

Again, it should be noted that comparison of Fig. 5.6 and Fig. 5.7 provides a clear insight to the effects of both interfacial height and position, with respect to the known receiver's position. Therefore, by displaying the TOF projection data in two different manners, both the interfacial height \( h \) and the position \( z_r \) can be readily distinguished for convex interface shapes when the receiver's position is located in the solid.
Figure 5.6  Ultrasonic time-of-flight projection data for convex interfaces, \( h = 2, 5, \) and 10 mm, for a receiver located in the solid at (a) \( z_r = -5 \) mm, (b) \( z_r = -10 \) mm, (c) \( z_r = -15 \) mm and (d) \( z_r = -20 \) mm.
Figure 5.7 Ultrasonic time-of-flight projection data for convex interfaces versus a constant receiver position (\( z_r = 0 \)) for interfacial heights of (a) \( h = 2 \) mm, (b) \( h = 5 \) mm, and (c) \( h = 10 \) mm.
5.4 Concave Interfaces ($h < 0$)

5.4.1 Receiver above interface ($z_r > 0$)

For concave interfaces, only direct and singly transmitted rays are observed. Table 5.3 shows the mathematical representation of the possible ray paths encountered for concave interfaces ($h < 0$) with the receiver located in the liquid ($z_r > 0$). The ultrasonic TOF projections for concave ($h = -2$ and -5 mm) interfaces are shown in Fig. 5.8(a) - (d) for a receiver located in the liquid ($z_s = 5, 10, 15$ and 20 mm), respectively. In Fig. 5.8 the TOF of rays generated in the solid ($z_s < 0$) corresponds to singly transmitted rays. When the source is located in the liquid ($z_s > 0$) only direct rays were observed. The TOF projection for the $h = -10$ mm interface was not shown because the magnitude of the dark zone extended beyond that of the scanned region (i.e. the singly transmitted wavefronts did not intersect the outer boundary in the scanned region, 40 mm > $z_s > -20$ mm). Both TOF projection sets show good agreement between the experimentally determined TOF's and the numerically simulated data predicted by the ray path models.

With the receiver located in the liquid, Fig. 5.8, the interface location may be deduced by the presence of a dark zone just below the interface or the absence of direct rays below the interface edge ($z_i = 0$). The TOF projections of direct rays in the liquid are constant for both interface convexities and shift accordingly with the receiver's position. However, the TOF data profiles of singly transmitted rays are shifted to the right (i.e. longer TOF's) as the interface convexity $h$ is increased negatively. This is also intuitive; as the negative convexity is increased the fraction of the total path length of the ray in the lower velocity liquid increases and the fraction in the higher velocity solid decreases resulting in an overall increase in TOF.
Table 5.3: Possible ray paths encountered for concave interfaces \( h < 0 \) with the receiver located in the liquid \( z_r > 0 \).

<table>
<thead>
<tr>
<th>Type of ( z_r )</th>
<th>( \tau_{nr} )</th>
<th>( \tau_{st} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>non refracted</td>
<td>( \sqrt{\frac{(x_r-x_s)^2 + (z_r-z_s)^2}{v_{liquid}}} )</td>
<td>( \sqrt{\frac{(x_1-x_s)^2 + (z_1-z_s)^2}{v_{solid}}} + \sqrt{\frac{(x_r-x_1)^2 + (z_r-z_1)^2}{v_{liquid}}} )</td>
</tr>
</tbody>
</table>

Again, it is interesting to note that as the receiver’s position was translated further from the interface edge \( (z_r = 5, 10, 15 \text{ and } 20 \text{ mm}) \) the overall TOF projection of singly transmitted rays for each interface convexity shifts to increased TOF values. The same two points are to be made about the magnitude of the dark zone with this sensing configuration. The overall magnitude of the dark zone increased with increasing convexity \( (h = -2, -5 \text{ to } -10 \text{ mm}) \) and the local magnitude for each individual interface decreased as the receiver’s position was translated further from the interface edge. It also appears that the rate of change with respect to the receiver’s position in dark zone magnitude is dependent on the interface convexity.

1. Cartesian coordinate system in mm. \( v_{liquid} = \text{liquid velocity (mm/}\mu\text{s)} \), \( v_{solid} = \text{solid velocity (mm/}\mu\text{s)} \).
The TOF projection data for concave interfaces versus a fixed receiver position ($z_r = 0$) for interfacial heights of -2 and -5 mm is shown in Fig. 5.9(a) and (b), respectively. In Fig. 5.9 the TOF of rays generated in the solid ($z_r < z_i$) corresponds to singly transmitted rays. When the source was located in the liquid ($z_r > z_i$) only direct rays were observed.

Comparison of Fig. 5.8 and Fig. 5.9 shows the effect of both the interfacial height and position with respect to the known receiver's position on the ultrasonic TOF projection data. It is clear from Fig. 5.8 that when the position of the interface edge is fixed ($z_i = 0$), the difference in interfacial height ($h$) can be readily observed for the two interfaces examined here. It can also be seen from Fig. 5.9 that when the receiver's position is fixed ($z_r = 0$), the relative position of the interface's edge ($z_i$) is readily observed. Therefore, by displaying the TOF projection data versus a fixed interface position ($z_i = 0$) or a fixed receiver position ($z_r = 0$), the effect of interfacial height ($h$) and interface position ($z_i$) can be readily observed for concave interface shapes when the receiver's position was located in the liquid.
Figure 5.8 Ultrasound time-of-flight projection data for concave interfaces, $h = -2$ and -5mm, for a receiver located in the liquid at (a) $z_r = 5$mm, (b) $z_r = 10$mm, (c) $z_r = 15$mm and (d) $z_r = 20$mm.
Figure 5.9 Ultrasonic time-of-flight projection data for concave interfaces versus a constant receiver position ($z_r = 0$) for interfacial heights of (a) $h = -2$ mm and (b) $h = -5$ mm.
5.4.2 Receiver below interface \((z_r < 0)\)

The ultrasonic TOF projections for concave \((h = -2 \text{ and } -5 \text{ mm})\) interfaces are shown in Fig. 5.10(a) - (d) for a receiver located in the solid \((z_r = -5, -10, -15 \text{ and } -20 \text{ mm})\), respectively. In Fig. 5.10 the TOF of rays generated in the solid \((z_f < 0)\) corresponds to direct rays. When the source was located in the liquid \((z_l > 0)\) only singly transmitted rays were observed. Again the TOF projection data for the \(h = -10 \text{ mm}\) interface convexity was not shown because the dark zone extended beyond that of the scanned region. Table 5.4 shows the mathematical representation of the possible ray paths encountered for concave interfaces \((h < 0)\) with the receiver located in the solid \((z_r < 0)\). Both TOF projection sets show good agreement between the experimentally determined TOF’s and the numerically simulated data predicted by the ray path models.

When the receiver is located in the solid, Fig. 5.10, the interface location is again readily identified by the presence of a dark zone just above the interface or the absence of direct rays above the interface edge \((z_i = 0)\). The TOF projection of direct rays in the solid are constant for both interface convexities and shift accordingly with receiver’s position. In the instance when no dark zone was observed the TOF of singly transmitted rays coincides with that of direct ray paths at \(z_i = 0\) for the interfaces. Again, the TOF data profiles of singly transmitted rays are shifted to longer TOF’s as the interface convexity \(h\) is increased negatively and/or as the receiver’s position was translated further from the interface edge. Also there are two important points to be made about the magnitude of the dark zone with this sensing configuration. The overall magnitude of the dark zone increased with increasing convexity \((h = -2, \text{ to } -5 \text{ mm})\) and the local magnitude for each individual interface decreased as the receiver’s position was translated further from the interface edge.
Table 5.4: Possible ray paths encountered for concave interfaces \((h < 0)\) with the receiver located in the solid \((z_r < 0)\).

<table>
<thead>
<tr>
<th>Type</th>
<th>Expression</th>
</tr>
</thead>
</table>
| singly transmitted | \[
\tau_{st} = \sqrt{\frac{(x_1 - x_s)^2 + (z_1 - z_s)^2}{v_{liquid}}} + \sqrt{\frac{(x_r - x_1)^2 + (z_r - z_1)^2}{v_{solid}}}
\] (5.8) |
| non refracted   | \[
\tau_{nr} = \sqrt{\frac{(x_r - x_s)^2 + (z_r - z_s)^2}{v_{solid}}}
\] (5.9) |

The TOF projection data for concave interfaces versus a fixed receiver position \((z_r = 0)\) for interfacial heights of -2 and -5 mm is shown in Fig. 5.10(a) and (b), respectively. In Fig. 5.10 the TOF of rays generated in the solid \((z_s < z_i)\) corresponds to singly transmitted rays. When the source was located in the liquid \((z_s > z_i)\) only direct rays were observed. Figure 5.10 shows good agreement between the experimentally determined TOF’s and the numerically simulated data predicted by the ray path model.

Again, it should be noted that comparison of Fig. 5.10 and Fig. 5.11 provides a clear insight to the effects of both interfacial height and position, with respect to the known receiver’s position. Therefore, by displaying the TOF projection data in two different manners, both the interfacial height \((h)\) and the position \((z_i)\) can be readily distinguished for concave interface shapes when the receiver’s position is located in the solid.

---

1. Cartesian coordinate system in mm. \(v_{liquid} = \) liquid velocity (mm/\(\mu\)s), \(v_{solid} = \) solid velocity (mm/\(\mu\)s).
Figure 5.10 Ultrasonic time-of-flight projection data for concave interfaces, \( h = -2 \) and -5mm, for a receiver located in the solid at (a) \( z_r = -5\text{mm} \), (b) \( z_r = -10\text{mm} \), (c) \( z_r = -15\text{mm} \) and (d) \( z_r = -20\text{mm} \).
Figure 5.11 Ultrasonic time-of-flight projection data for concave interfaces versus a constant receiver position ($z_r = 0$) for interfacial heights of (a) $h = -2$ mm and (b) $h = -5$ mm.
5.5 Planar Interface \((h = 0)\)

5.5.1 Receiver above interface \((z_r > 0)\)

The TOF projection data for a planar interface (receiver located in the liquid) versus a fixed interface position, \(z_i = 0\) and a fixed receiver position, \(z_r = 0\) is shown in Fig. 5.12(a) and (b), respectively. Because the planar interface is the degenerative case between the convex and concave interface shapes, it is intuitive that when rays were generated and detected in the same media, only direct rays were observed and when rays were generated and detected in different media, only singly transmitted rays were observed. In addition, no dark zones are present for planar interfaces. It is clear from Fig. 5.12 that the interface position is clearly defined by the transition of direct to singly transmitted rays. This effect can be readily seen whether the TOF projection data is plotted with a fixed interface position, Fig. 5.12(a) or a fixed receiver position, Fig. 5.12(b). Table 5.5 shows the possible ray paths encountered for a planar interface \((h \leq 0)\) with the receiver located in the liquid \((z_r > 0)\).

5.5.2 Receiver below interface \((z_r < 0)\)

The TOF projection data for a planar interface (receiver located in the solid) versus a) a fixed interface position, \(z_i = 0\) and b) a fixed receiver position, \(z_r = 0\) is shown in Fig. 5.13(a) and (b), respectively. It is clear from Fig. 5.13 that the interface position is clearly defined by the transition of direct to singly transmitted rays. This effect is not readily observed when the TOF projection data is plotted with a fixed interface position, Fig. 5.13(a), however it is readily observed when the data is plotted with a fixed receiver position, Fig. 5.13(b). Table 5.6 shows the possible ray paths encountered for a planar interface \((h = 0)\) with the receiver located in the solid \((z_r < 0)\).
Figure 5.12 Ultrasonic time-of-flight projection data for a planar interface (receiver located in the liquid) versus a) a fixed interface position, $z_l = 0$ and b) a fixed receiver position, $z_r = 0$. 
Figure 5.13 Ultrasonic time-of-flight projection data for a planar interface (receiver located in the solid) versus a) a fixed interface position, $z_i = 0$ and b) a fixed receiver position, $z_r = 0$. 
Table 5.5: Possible ray paths encountered for a planar interface \((h = 0)\) with the receiver located in the liquid \((z_r > 0)\).

\[
\tau_{nr} = \sqrt{\frac{(x_r - x_s)^2 + (z_r - z_s)^2}{v_{\text{liquid}}}}
\]

\[
\tau_{st} = \sqrt{\frac{(x_1 - x_s)^2 + (z_1 - z_s)^2}{v_{\text{solid}}}} + \sqrt{\frac{(x_r - x_1)^2 + (z_r - z_1)^2}{v_{\text{liquid}}}}
\]

Table 5.6: Possible ray paths encountered for a planar interface \((h = 0)\) with the receiver located in the solid \((z_r < 0)\).

\[
\tau_{st} = \sqrt{\frac{(x_1 - x_s)^2 + (z_1 - z_s)^2}{v_{\text{liquid}}}} + \sqrt{\frac{(x_r - x_1)^2 + (z_r - z_1)^2}{v_{\text{solid}}}}
\]

\[
\tau_{nr} = \sqrt{\frac{(x_r - x_s)^2 + (z_r - z_s)^2}{v_{\text{solid}}}}
\]

1. Cartesian coordinate system in mm. \(v_{\text{liquid}}\) = liquid velocity (mm/\(\mu\)s), \(v_{\text{solid}}\) = solid velocity (mm/\(\mu\)s).
5.6 Discussion

An inspection of the ultrasonic TOF projection data reveals that both the magnitude and form of TOF curves are different for different sensing configurations and interfacial curvatures. The TOF projection data reveals that a solid-liquid interface does exist. This is denoted by either a transition in propagation modes (i.e. doubly transmitted rays to singly transmitted rays or singly transmitted rays to direct rays) or the observance of dark zones at the interface edge \( z_i = 0 \). Determining whether the interface is above or below the receiver point can be easily done by inspecting the TOF curves. For either convex or concave interfaces, the TOF curves for direct rays will be symmetric about the receiver point and much larger when the receiver is positioned in the slower velocity liquid. Also, if we compare convex and concave interfaces, we find that for a convex interface the TOF of transmitted rays (both singly and doubly) increases with decreasing interface convexity, while for a concave interface the TOF of singly transmitted rays decreases with decreasing interface convexity.

5.7 Non-Linear Least Squares Reconstruction

There are a variety of techniques available for reconstructing an object image from ultrasonic TOF projection data, including nonlinear least squares fitting, algebraic reconstruction techniques (ART) and convolution backprojection (CB) methods [102,103]. Convolution backprojection methods have not been applied to situations where ray bending is significant, and although algebraic reconstruction techniques are beginning to incorporate ray bending [104], both these procedures require large data sets. Reconstruction approaches that can be used with limited data and exploit the often significant a priori information available are preferable. The crystal grower requires only the axial location
(z_i) of the interface (its change with time gives the solidification velocity) and its approximate curvature (h). The liquid and solid velocities (ν_l, ν_s) are also sought since they are related to the local temperature, composition and the crystals crystallographic orientation.

We assume the model geometry is of the form shown in Fig. 4.1, where h, z_p, ν_l and ν_s are all unknown. For the model, the TOF depends nonlinearly on the interface convexity (h), interface position (z_i), liquid (ν_l) and solid (ν_s) velocities and the mean-square error is given by

\[ \chi^2 = \sum_{i=1}^{M} [\tau_i - \hat{\tau}_i(x_i; h, z_i, \nu_l, \nu_s)]^2 \]  

(5.14)

where τ_i are the measured time-of-flights and \( \hat{\tau}_i \) are the predicted time-of-flights for a model estimate of the interface. To reconstruct the model unknowns from the fan beam TOF projection data a Levenberg-Marquardt nonlinear least-squares reconstruction method was used [105]. The nonlinear least-squares method determines the best-fit parameters \( (h, z_p, \nu_l, \nu_s) \) by minimizing \( \chi^2 \). A schematic flow chart of the non linear least squares reconstruction algorithm is shown in Fig. 5.14.
Figure 5.14 Flow chart of the non linear least squares reconstruction algorithm.
We first examine the reconstruction results for convex interfaces. The reconstructed interface locations and curvatures when the receiver is above the interface are shown in Fig. 5.15(a) - (c) for convex interfaces $h = 2, 5$ and $10$ mm, respectively. The reconstructed parameters obtained when the receiver is below the interface are shown in Fig. 5.16(a) - (c). It is clear that the reconstructed interface locations and curvatures coincide well with those of the actual interfaces. For the reconstructed velocities, the mean liquid velocity was $v_l = 1.487$ ($\sigma = 0.040$) and the mean solid velocity was $v_s = 2.677$ ($\sigma = 0.037$).

The reconstructed interface locations and curvatures when the receiver is above the interface are shown in Fig. 5.17(a) and (b) for concave interfaces $h = -2$ and $-5$ mm, respectively. The reconstructed parameters obtained when the receiver is below the interface are shown in Fig. 5.18(a) and (b). Again the reconstructed interface locations and curvatures coincide well with those of the actual interfaces. For the reconstructed velocities, the mean liquid velocity was $v_l = 1.487$ ($\sigma = 0.040$) and the mean solid velocity was $v_s = 2.677$ ($\sigma = 0.037$).

Therefore, the nonlinear least-squares reconstruction algorithm represents a robust approach for interface reconstructions using ultrasonic TOF projection data. Using the boundary value solutions with free parameters $(h, z_p, v_l, v_s)$ the reconstruction algorithm converged upon the correct interface model (convex or concave), and thus recovered the interface geometry (i.e. solid-liquid interface location, curvature) and velocity fields for all interface convexities from laser ultrasonic TOF projection data collected in the diametrical plane.
Figure 5.15 Non-linear least squares interface reconstructions for convex interfaces with the receiver located in the liquid for interface heights of (a) $h = 2$ mm, (b) $h = 5$ mm, and (c) $h = 10$ mm.
Figure 5.16 Non-linear least squares interface reconstructions for convex interfaces with the receiver located in the solid for interface heights of (a) $h = 2$ mm, (b) $h = 5$ mm, and (c) $h = 10$ mm.
Figure 5.17 Non-linear least squares interface reconstructions for concave interfaces with the receiver located in the liquid for interface heights of (a) \( h = -2 \) mm, and (b) \( h = -5 \) mm.
Figure 5.18 Non-linear least squares interface reconstructions for concave interfaces with the receiver located in the solid for interface heights of (a) $h = -2$ mm, and (b) $h = -5$ mm.
5.8 Summary

A combination of ray tracing, wavefront analysis and TOF analysis of wave propagation in a model isotropic solid-liquid interfaces has been used in combination with experimental testing with a laser ultrasonic sensing system to evaluate the validity of determining a solid-liquid interface’s location, curvature and local velocity fields from ultrasonic TOF projection data collected in the diametral plane. The results indicated that because convex and concave solid-liquid interfaces resulted in uniquely different TOF data profiles, the interface shape (convex or concave) was readily determined from the TOF data. When the TOF data (~10 - 60 rays) collected in the diametral plane was used in conjunction with a nonlinear least squares reconstruction algorithm, the interface geometry (i.e. location and curvature) was successfully reconstructed and the ultrasonic velocities of both solid and liquid obtained.
Chapter 6

Elastic Properties of (Cd,Zn)Te

The emergence of optical (laser) methods for the remote excitation and detection of ultrasound now enables these transmission approaches to be extended to vertical Bridgman configurations. However reliable elastic constant and density data as a function of temperature are needed in order to realize the potential of these laser ultrasonic sensing approaches. The temperature dependence of the linear thermal expansion for both solid and liquid CdTe have been previously determined by Williams et al. [116] and Glazov et al. [117]. While some data relating the elastic constants of CdTe to temperature exists for low temperatures (<300K), [89,118] none has been published for the elevated temperatures encountered during crystal growth and the role of Zn in (Cd,Zn)Te alloys has also not been established.

6.1 Introduction

Elastic constants at ambient temperatures or below are often determined by ultrasonic methods. Both resonance methods and pulse-echo methods have been used [119]. However both methods conventionally use piezoelectric transducers to excite/detect ultra-
sound and are therefore experimentally difficult at high temperatures since they require buffer rods, cooling systems, special bonds or momentary contact to keep piezoelectric transducers below their Curie point. The problem is further compounded by the high vapor pressure of Cd in CdTe alloys as they approach their melting point [120]. This requires encapsulation in thick ampoules and precludes direct contact with the transducers. Here it is shown that measurement at high temperatures can be accomplished quite readily on quartz encapsulated samples by the use of laser ultrasonics which uses lasers to non-invasively generate and detect ultrasound.

In this chapter, the temperature dependence of the ultrasonic velocity for solid and liquid Cd$_{0.96}$Zn$_{0.04}$Te contained in quartz ampoules with very small free volumes has been deduced from time-of-flight data collected in primary low index orientations. Using these velocity values together with data for the temperature dependent density allows a complete evaluation of the single crystal elastic stiffness constants ($C_{11}$, $C_{12}$, $C_{44}$) and polycrystalline elastic stiffness constants ($E$, $K$, $G$) for solid and the adiabatic bulk modulus ($K_S$) for liquid Cd$_{0.96}$Zn$_{0.04}$Te.

### 6.2 Inversion Techniques

The most straightforward and precise method for evaluating the elastic stiffness constants of anisotropic solids, is through the measurement of the ultrasonic velocity of pure longitudinal and pure shear modes propagating in principal symmetry directions, *i.e.* (100), (110) and (111) for cubic materials. Cadmium telluride and its substitutional solid solution (Cd,Zn)Te alloys have a zinc-blende (cubic) structure. It can be shown from Eqn. (3.6) and (3.7), that the three bulk wave velocities (one longitudinal and two shear) can be expressed as a function of the elastic stiffness constants $C_{11}$, $C_{12}$, $C_{44}$ and the density $\rho$. 

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Table 3.1 gives the expressions for the pure longitudinal and pure shear velocities in the primary \( \langle 100 \rangle \), \( \langle 110 \rangle \) and \( \langle 111 \rangle \) directions for a cubic crystal structure. Note, that the two shear wave velocities are equivalent in both \( \langle 100 \rangle \) and \( \langle 111 \rangle \) directions. Moreover it can be shown that in all cases in Table 3.1, except the shear wave in the \( \langle 111 \rangle \) direction, the energy flux vector is in the same direction as the wave normal [88]. Thus the measurement of three velocities that are independently related to \( C_{11} \), \( C_{12} \) and \( C_{44} \) allows the determination of the three elastic stiffness constants. The longitudinal wave velocity in the \( \langle 111 \rangle \) and \( \langle 100 \rangle \) directions and the shear wave velocity in the \( \langle 100 \rangle \) direction have been chosen to evaluate the three elastic stiffness constants. The longitudinal wave velocity in the \( \langle 110 \rangle \) direction could have also been used, however, it was chosen as a self consistent check of the single crystal elastic stiffness constants. The following relations were used:

\[
C_{11} = \rho v_l^2[100] \tag{6.1}
\]

\[
C_{44} = \rho v_s^2[100] \tag{6.2}
\]

\[
C_{12} = 0.5 \rho (3v_l^2[111] - v_l^2[100] - 4v_s^2[100]) \tag{6.3}
\]

and

\[
C_{12} = \rho (2v_l^2[110] - v_l^2[100] - 2v_s^2[100]) \tag{6.4}
\]

where \( v_l \) and \( v_s \) are the pure longitudinal and shear wave velocities, respectively.
6.3 Thermal Linear Expansion and Density of CdTe

In the solid state, the sample’s thickness and thus density are governed by the linear thermal expansion. Williams et al. [116] and Glazov et al. [117] have reported data for the temperature dependence of the linear thermal expansion and density for CdTe. Glazov et al. [121] reported density data calculated from

\[ \rho_t = \frac{\rho_r}{(1 + \Delta l_r)^3} \]  \hspace{1cm} (6.5)

where \( \rho_t \) is the density at a given temperature, \( \rho_r \) is the density at room temperature and \( \Delta l_r \) is the elongation per 1 cm length of the sample due to heating. A reported room temperature density of 5.80 g/cm\(^3\) for CdTe was used, which is slightly lower that the now accepted value of 5.854 g/cm\(^3\) [90]. Figure 6.1 shows the data for the linear thermal expansion for solid CdTe of both Williams [116] and Glazov et al. [117]. The data in Fig. 6.1 is well fitted by a quadratic relationship:

\[ \frac{\Delta l_r}{l_0}(\%) = -0.01918 + 5.5735 \times 10^{-4} T + 4.1866 \times 10^{-8} T^2 \]  \hspace{1cm} (6.6)

where \( T \) is the temperature (in °C). Subsequently, the thermal expansion coefficient, \( \alpha \), of CdTe can be evaluated by differentiation of Eqn. (6.6) with respect to temperature (note a change from °C to K) and is obtained in the linear form

\[ \alpha(K^{-1}) = 5.345 \times 10^{-6} + 8.373 \times 10^{-10} T \]  \hspace{1cm} (6.7)

where \( T \) is the absolute temperature. At room temperature \( \alpha \) is 5.59 \times 10^{-6} K\(^{-1}\) which is comparable to 4.96 \times 10^{-6} K\(^{-1}\) reported by Williams et al. [116].
Figure 6.1 Temperature dependence of the thermal linear expansion ($\Delta l/l_0$) for CdTe; data taken from Williams et al. [116] and Glazov et al. [117].

Substituting Eqn. (6.6) and a room temperature density of 5.854 g/cm$^3$ into Eqn. (6.5) the corrected values for the density were evaluated. Figure 6.2 shows both the corrected and original data for the temperature dependence of the density for CdTe in the solid and liquid phases. Also shown in Fig. 6.2 (using Eqn. (6.5)) is a quadratic fit for solid CdTe represented by

$$\rho (g/cm^3) = 5.8574 - 9.7826 \times 10^{-5} T - 6.3005 \times 10^{-9} T^2,$$

(6.8)

and a linear fit for liquid CdTe represented by

$$\rho (g/cm^3) = 5.8287 - 1.4337 \times 10^{-4} T$$

(6.9)

where $T$ is the temperature (in °C). For the work here it is assumed that the linear thermal expansion and density for CdTe and Cd$_{0.96}$Zn$_{0.04}$Te are the same.
Evaluating Eqns. (6.8) and (6.9) with a melting point of 1098°C [122] for 
Cd_{0.96}Zn_{0.04}Te results in a solid density of 5.742 g/cm³ and a liquid density of 5.671 
g/cm³ at the melting point. Thus, the density of the liquid phase is \(~1.24\%\) lower than the 
density of the solid phase, consistent with a semiconductor \(\rightarrow\) semiconductor type of 
melting, \textit{i.e.} one in which covalent characteristics of the bond are partially preserved during 
melting [123]. It has been speculated that the covalent nature in the molten state is likely 
to be retained as one-dimensional chain-like or molecular structures or in some temperature 
regions as two-dimensional units [123]. As a result, semiconductors such as CdTe 
which retain their chemical bonding in the liquid state exhibit an expansion at the melting 
point, which is due to increases in the average interatomic distances and in the number of 
defects (primarily vacancies) [117]. This is further supported by the fact that the electrical 
conductivity increases exponentially with temperature in the molten state [73].

In the liquid state, the sample thickness is defined by the internal diameter of the 
quartz ampoule which contains the charge. Figure 6.3 shows the data for the thermal linear 
expansion for quartz [121]. The data in Fig. 6.3 is well fitted by a quadratic relationship:

\[
\frac{\Delta l}{l_0}(\%) = -0.01897 + 6.4966 \times 10^{-5} T + 8.0884 \times 10^{-9} T^2
\]  

(6.10)

where \(T\) is the temperature (in °C).
Figure 6.2 Temperature dependence of the density ($\rho$) for CdTe; data taken from Williams et al. [116] and Glazov et al. [117].

Figure 6.3 Temperature dependence of the thermal linear expansion ($\Delta l/l_0$) for quartz [121].
6.4 Experimental Procedure

6.4.1 Laser Ultrasonic Measurement Technique

Ultrasonic time-of-flight’s (TOF’s) between precisely positioned source and receiver points were measured using the laser ultrasonic system shown in Fig. 6.4. A ~10 ns duration Q-switched Nd:YAG laser pulse of 1.064-μm wavelength was used as the ultrasonic source. The energy per pulse was ~10 mJ and the roughly Gaussian beam of the multimode pulse was focused to an approximate circular spot of 2 mm diameter. Thus, the source power density was ~100 MW/cm². Although this was slightly in the ablative regime, minimal surface damage incurred during repeated pulsing. In addition, the quartz ampoule provided a constrained surface resulting in large amplitude longitudinal and shear waves.

The ultrasonic receiver was a Mach-Zehnder heterodyne laser interferometer. It responded to the sample’s out-of-plane (normal) surface displacement associated with wavefront arrivals at the receiver point. It was powered by a 5 mW HeNe laser which produced a continuous Gaussian beam of 632.8-nm wavelength focused to a circular spot ~100 μm in diameter. The interferometer had a displacement sensitivity of 0.4 Å/mV and exhibited linear output for displacements up to about 300 Å. For the experiments reported here, maximum surface displacements were on the order of 200 Å. The signal from the interferometer was bandpass filtered between 10 kHz and 10 MHz and recorded with a precision digital oscilloscope at a 2 ns sampling interval using 8-bit analog-to-digital conversion. To improve the signal-to-noise ratio, each waveform used for a TOF measurement was the average of ~50 pulses collected at a pulse repetition rate of 20 Hz. A fast photodiode identified the origination time for the ultrasonic signals.
Figure 6.4 A schematic illustration of the high temperature laser ultrasonic test facility used to evaluate the temperature dependence of the elastic properties.
6.4.2 Sample Preparation and Test Methodology

Cd$_{0.96}$Zn$_{0.04}$Te samples were supplied by Johnson Matthey Electronics (Spokane, WA). The material consisted of precompounded IRFPA substrate purity polycrystalline equatomic CdTe to which Zn and Te was added to reach the target zinc concentration of 4 at.\% ± 1\%. The subsequent precompounded ingot was then grown from the melt using a commercial 17-zone VB growth furnace and “mined” into samples that measured $10 \times 10 \times 5$ mm$^3$ in size. The samples were mined so that the thickness (5mm) was oriented in the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. One surface was lapped and the other chemical-mechanical polished to provide a reflective surface for the laser interferometer. They were contained in 10 mm ID square quartz ampoules with quartz plugs (to fill in the free volume) and sealed under $10^{-6}$ torr with a very small free volume to inhibit the vaporization of Cd during subsequent heating, Fig. 6.5(a). Ingots for liquid state measurements were prepared in the same manner, except that the polycrystalline ingot (~350 g) was contained in a 30 mm ID quartz ampoule, Fig. 6.5(b).

Heating was accomplished with a programmable tubular furnace. The furnace was equipped with a temperature controller that was able to maintain the temperature to within 1°C. The Cd$_{0.96}$Zn$_{0.04}$Te samples were supported by a Al$_2$O$_3$ support assembly. The laser source and receiver gained access into the furnace through small (~4 mm) slits at each end of the furnace. The sample temperature was measured with two type R thermocouples: one located on the generation side of the sample and the other on the receiver side. In both cases, the thermocouples were in physical contact with the outer surface of the ampoule and shielded from the direct heat source. Variations of the temperature in the region of the sample was better than ±1°C. The solid samples were heated at a rate of 2°C/min. and allowed to equilibrate ~30 min. at each test temperature (every 25°C). The liquid sample was heated at a rate of 10°C/min. up to 1070°C and allowed to equilibrate at this tempera-
ture for several hours. Subsequent cyclic heating and cooling near the melting temperature was conducted at a rate of 1°C/min. in 5°C increments and allowed to equilibrate for ~1 hour at each test temperature.

Figure 6.5  A schematic illustration of the sample configurations for (a) solid and (b) liquid Cd$_{0.96}$Zn$_{0.04}$Te (all dimensions in mm).
6.5 Time of Flight and Velocity Analysis

6.5.1 Wavefront Identification

Figure 6.6 shows the normal displacement waveforms measured at ambient temperatures (~21°C) of samples oriented in \( \langle 100 \rangle \), \( \langle 110 \rangle \) and \( \langle 111 \rangle \) directions. For any material (isotropic or anisotropic), unambiguous identification of the arrival times is a prerequisite to any TOF measurement. However, identification from comparison to the theoretical waveforms of Fig. 6.6 is difficult, since CdTe and its alloys are anisotropic. Calculation of the theoretical waveforms is beyond the scope of this chapter and would require calculation of the Green function for a material of cubic symmetry. Therefore the arrival times of the bulk ultrasonic waves have been identified using values for the velocities, Table 3.1, calculated from published elasticity and density data \( C_{11} = 53.30 \text{ GPa}, C_{12} = 36.50 \text{ GPa and } C_{44} = 20.44 \text{ GPa and } \rho_s = 5.854 \text{ gm/cm}^3 \) [89,118].

Fig. 6.6(a) shows the normal surface displacement waveform in the \( \langle 100 \rangle \) direction. The interferometer output shows two distinct wavefront arrivals. The first arrival (1L) corresponds to that of the longitudinal wave and the second (1S) to that of the shear wave. In Fig. 6.6(b), \( \langle 110 \rangle \) direction, the first (1L) and third (3L) reflections of the longitudinal wave along with the fast (FS) and slow (SS) shear wave arrivals were observed. In the \( \langle 111 \rangle \) direction, Fig. 6.6(c), only the first (1L), third (3L) and fifth (5L) reflections of the longitudinal wave were observed. No shear wave arrival was observed because the energy flux vector is not in the same direction as the wave normal [88]. In all cases the start time of the ultrasonic wavefront is denoted by the photodiode pulse.
Figure 6.6 Typical ultrasonic waveforms denoting the arrival TOF of the longitudinal and shear waves in (a) ⟨100⟩, (b) ⟨110⟩ and (c) ⟨111⟩ crystal orientations for solid Cd₀.₉₆Zn₀.₄₄Te at 21°C.
The normal displacement waveform measured in the liquid state (1140°C) is shown in Fig. 6.7. The waveform shows two distinct arrival events. During laser ultrasonic generation the thermal expansion of the liquid induces a force at the constrained liquid-quartz interface generating an energetic elastic wave in the quartz ampoule. This wave propagates circumferentially in the ampoule with a velocity corresponding to that of a zeroth-order symmetric Lamb wave in quartz. The arrival of this encircling wave is indicated by the minor surface displacement at ~8 µs. The second event at ~23 µs is due to the arrival of the longitudinal wave propagating through the liquid along a straight path from the source to the receiver. In Fig. 6.7 the photodiode pulse denotes the start time for the ultrasonic signals.

![Graph showing ultrasonic waveforms](image)

**Figure 6.7** Typical ultrasonic waveform denoting the arrival TOF of the encircling and longitudinal waves in liquid Cd_{0.96}Zn_{0.04}Te at 1140°C.
6.5.2 Ultrasonic Time-of-Flight and Velocity

The temperature dependence of the ultrasonic velocity was evaluated from the measured TOF data of longitudinal waves in $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ orientations and the shear wave in the $\langle 100 \rangle$ orientation. The ingots' instantaneous length was calculated from Eqn. (6.6) at each target temperature. The measured temperature dependence of the longitudinal wave velocity in $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ orientations is shown in Fig. 6.8. Errors in the measured longitudinal wave velocities were within $\pm 0.02 \text{ mm/\mu s}$. The measured temperature dependence of the shear wave velocity in the $\langle 100 \rangle$ orientation is shown in Fig. 6.9. Errors in the measured shear wave velocities were within $\pm 0.01 \text{ mm/\mu s}$. Both the longitudinal and shear waves showed a monotonically decreasing velocity with temperature. The existence of CdTe crystals of a hexagonal structure at high temperatures has been reported [124-126]. It has been speculated that CdTe can easily oscillate between hexagonal and cubic structures near its liquid/solid transition temperature during growth processes from congruent melts [3]. However, no evidence of $\text{solid} \rightarrow \text{solid}$ phase changes or other anomalous effects was observed in the ultrasonic velocity data collected near the melting point.

In the liquid state, the TOF was measured during both heating and cooling. The longitudinal wave velocity was then calculated assuming that the ingot diameter is governed by the thermal expansion of the quartz ampoule, Eqn. (6.10). The temperature dependence of the longitudinal wave in the liquid state is shown in Fig. 6.10. Errors in the measured longitudinal wave velocities were within $\pm 0.002 \text{ mm/\mu s}$. As the temperature increased there was a loosening of the covalent (semiconducting) liquid structure due to thermal motion with a concomitant linear drop in the longitudinal wave velocity in the temperature region monitored. No evidence of liquid-liquid polymorphisms or other anomalies was observed in the liquid velocity data.
The ultrasonic velocity data for the solid and liquid phases was well fitted by quadratic relationships. Table 6.1 shows the quadratic fits for the temperature dependence for the ultrasonic velocities in both the solid and the liquid phases from Figs. 6.8, 6.9 and 6.10. Both the longitudinal and shear wave velocities exhibited a strong monotonically decreasing function of temperature in the solid and liquid phases. The longitudinal wave velocity was found to be ~2 times faster in the solid phase (depending on the crystallographic orientation) at the melting temperature, Fig. 6.11. This ultrasonic velocity ratio \( v_{\text{sol}}/v_{\text{liq}} \) between the solid and liquid phases appears to be sufficient for the implementation of laser ultrasonic sensors to monitor the liquid-solid interface during vertical Bridgman growth.

![Graph showing temperature dependence of wave velocity](image)

**Figure 6.8** Temperature dependence of the quasi-longitudinal wave velocity in \( \langle 100 \rangle \), \( \langle 110 \rangle \) and \( \langle 111 \rangle \) orientations for solid Cd\(_{0.96}\)Zn\(_{0.04}\)Te.
Figure 6.9 Temperature dependence of the quasi-shear wave velocity in the \( \langle 100 \rangle \) orientation for solid \( \text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te} \).

Figure 6.10 Temperature dependence of the longitudinal wave phase velocity in liquid \( \text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te} \).
Table 6.1: Temperature dependent polynomial fits of the longitudinal and shear wave velocity data of \( \text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}. \)

<table>
<thead>
<tr>
<th>Type of Wave</th>
<th>Orientation</th>
<th>Temperature Dependent Velocity (mm/μs) ( T = ^\circ\text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal</td>
<td>\langle 100\rangle</td>
<td>( 3.0669 - 1.9166\times10^{-4}T - 1.9325\times10^{-7}T^2 )</td>
</tr>
<tr>
<td>Longitudinal</td>
<td>\langle 110\rangle</td>
<td>( 3.3558 - 2.5281\times10^{-4}T - 1.1719\times10^{-7}T^2 )</td>
</tr>
<tr>
<td>Longitudinal</td>
<td>\langle 111\rangle</td>
<td>( 3.4533 - 2.4453\times10^{-4}T - 1.3436\times10^{-7}T^2 )</td>
</tr>
<tr>
<td>Shear</td>
<td>\langle 100\rangle</td>
<td>( 1.8587 - 1.2779\times10^{-4}T - 3.6514\times10^{-8}T^2 )</td>
</tr>
<tr>
<td><strong>Liquid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal</td>
<td></td>
<td>( 1.8984 - 5.0801\times10^{-4}T )</td>
</tr>
</tbody>
</table>

![Graph showing wave velocity changes with temperature](image)

**Figure 6.11** The effect of melting on the quasi-longitudinal wave velocity for solid and liquid \( \text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}. \) The solid quasi-longitudinal velocity data was taken from a polycrystalline ingot.
6.6 Elastic Stiffness Constants

6.6.1 Single Crystal Elastic Constants

The temperature dependent single crystal elastic stiffness constants for the solid phase can be deduced from ultrasonic velocities measured in the three primary crystal directions and published temperature dependent density using the simple inversion formula summarized in Eqns. (6.1) - (6.4). The temperature dependence of the solid phase elastic stiffness constants ($C_{11}$, $C_{12}$, and $C_{44}$) is shown in Fig. 6.12. Like the ultrasonic velocity data, the elastic stiffness constants exhibited a monotonically decreasing function of temperature. The adiabatic bulk modulus ($K_S$) for the liquid state can be evaluated from liquid velocity data and is shown in Fig. 6.13. Table 6.2 shows polynomial fits for the temperature dependence of the elastic constants in both the solid and the liquid phases.

![Graph showing the temperature dependence of the single crystal elastic stiffness constants ($C_{11}$, $C_{12}$ and $C_{44}$) for solid Cd$_{0.96}$Zn$_{0.04}$Te.](image-url)
Figure 6.13 Temperature dependence of the bulk modulus ($K_S$) for liquid Cd$_{0.96}$Zn$_{0.04}$Te.

Table 6.2: Temperature dependent polynomial fits of the single crystal elastic stiffness constant data of Cd$_{0.96}$Zn$_{0.04}$Te.

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Temperature Dependent Elastic Property (GPa) $T = ^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid</strong></td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>$55.166 - 8.4965 \times 10^{-3} T - 5.2918 \times 10^{-6} T^2$</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>$36.785 - 6.7152 \times 10^{-3} T - 2.2293 \times 10^{-6} T^2$</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>$20.242 - 3.1824 \times 10^{-3} T - 5.4288 \times 10^{-7} T^2$</td>
</tr>
<tr>
<td><strong>Liquid</strong></td>
<td></td>
</tr>
<tr>
<td>$K_S$</td>
<td>$18.879 - 7.9113 \times 10^{-3} T$</td>
</tr>
</tbody>
</table>
The single crystal elastic stiffness constants \((C_{11}, C_{12}, C_{44})\) for solid and the adiabatic bulk modulus \((K)\) for liquid of \(Cd_{0.96}Zn_{0.04}Te\) have been fully evaluated from 20 - 1140°C covering the broad spectrum of temperatures encountered during vertical Bridgman growth. In addition the phase and group velocities of the three bulk wave modes can be evaluated for any crystallographic orientation and temperature. This data is a necessary prerequisite in accurate model development of laser ultrasonic sensing methodologies to monitor the solid-liquid interface position and shape during VB solidification.

6.6.2 Polycrystalline Elastic Constants

Due to the fact that CdTe and its alloys rarely solidify as a single crystal, it is also necessary to evaluate polycrystalline elastic moduli. This data can be used to approximate quasi-isotropic wave propagation in polycrystalline alloys. Methods for averaging the single crystal elastic stiffness constants \((C_{11}, C_{12}, C_{44})\) for cubic materials to obtain effective values for polycrystalline elastic constants are important in determining the ultrasonic behavior of polycrystalline materials. These isotropic polycrystalline elastic constants include Young’s modulus \((E)\), the bulk modulus \((K)\), the shear modulus \((G)\), Lame’ constants \((\lambda, \mu)\) and Poisson’s ratio \((\nu)\). Several authors [128-132] have proposed methods to estimate polycrystalline moduli and several thorough reviews have been published by Ledbetter [133], Hearmon [134] and Hashin [135].

The elastic properties of polycrystalline bodies depends on the macroscopic behavior of a polycrystalline body’s individual single crystals (crystallites or grains). In principle, the averaging problem can be solved by considering simultaneously the elastic equilibrium equations for each grain together with the boundary conditions at grain interfaces; in practice, this approach poses insurmountable problems [127].

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Most averaging methods assume, either explicitly or implicitly, certain conditions in the polycrystalline body [127]:

- The number of grains comprising the body is sufficiently large.
- Grains are randomly oriented; that is preferred orientations are absent.
- Grains sizes do not vary so much that a few orientations contribute dominantly.
- Grains are not so small that their crystallinity is lost.
- Elastic stiffnesses are homogeneous within a grain and between crystallites.
- Grain boundaries per se contribute nothing to the body elastic properties.

For materials with a cubic symmetry, the averaging problem consists of reducing the three independent elastic stiffness coefficients to two independent constants that describe completely the elastic behavior of quasi-isotropic solids, those solids whose properties are anisotropic locally but isotropic macroscopically [127]. The bulk modulus $(K)$ is a scalar invariant of the elastic stiffness tensor and is represented by

\[
K = \frac{1}{3}(C_{11} + 2C_{12})
\]  
(6.11)

It is assumed that the polycrystal and single crystal bulk moduli are equal and therefore the grain boundaries contribute nothing to the polycrystalline elastic properties.

The problem remains, then, to determine a second polycrystalline elastic stiffness constant. The second constant cannot be chosen uniquely. Generally, Young’s modulus $(E)$ and the shear modulus $(G)$ are often calculated. The most straightforward of the averaged
quantities are the Voight \((E_V \text{ and } G_V\) homogeneous strain) \([128,129]\) and the Reuss \((E_R \text{ and } G_R, \text{homogeneous stress}) \([130]\) averages given by

\[
E_R = \frac{5C_{44}(C_{11}-C_{12})(C_{11}+2C_{12})}{C_{11}^2 + C_{11}C_{12} - 2C_{12}^2 + 3C_{44}C_{11} + C_{44}C_{12}} 
\tag{6.12}
\]

\[
G_R = \frac{5C_{44}(C_{11}-C_{12})}{4C_{44} + 3(C_{11}-C_{12})} \tag{6.13}
\]

\[
E_V = \frac{(C_{11}-C_{12} + 3C_{44})(C_{11} + 2C_{12})}{2C_{11} + 3C_{12} + C_{44}} \tag{6.14}
\]

\[
G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \tag{6.15}
\]

Hill \([136]\) states the \((E_V \text{ and } E_R)\) and \((G_V \text{ and } G_R)\) are upper and lower bounds for the polycrystalline moduli obtained from the single crystal elastic stiffness constants and suggests two approximations;

\[
E_{VR-a} = \frac{1}{2}(E_V + E_R) \tag{6.16}
\]

\[
E_{VR-g} = \sqrt{E_V E_R} \tag{6.17}
\]

where \(E_{VR-a}\) and \(E_{VR-g}\) represent the arithmetic and geometric averages. The same arithmetic and geometric averaging can be applied to the shear modulus \((G_{VR-a} \text{ and } G_{VR-g})\):

\[
G_{VR-a} = \frac{1}{2}(G_V + G_R) \tag{6.18}
\]

\[
G_{VR-g} = \sqrt{G_V G_R} \tag{6.19}
\]
Now the polycrystalline elastic moduli can be calculated from the single crystal elastic stiffness constants for Cd$_{0.96}$Zn$_{0.04}$Te. The calculated temperature dependent polycrystalline elastic stiffness moduli for Young’s and the shear moduli (Eqns. (6.12) - (6.19)) are shown in Fig. 6.14. In Fig. 6.14, the arithmetic and geometric means of the Voight and Reuss models are sufficiently equivalent that only the arithmetic mean is shown. Table 6.3 shows polynomial fits for the temperature dependence of the polycrystalline elastic moduli of Cd$_{0.96}$Zn$_{0.04}$Te.

![Figure 6.14 Temperature dependence of the Voight and Reuss polycrystalline elastic moduli (E and G) for solid Cd$_{0.96}$Zn$_{0.04}$Te.](image)
Table 6.3: Temperature dependent polynomial fits of the polycrystalline elastic moduli data of Cd$_{0.96}$Zn$_{0.04}$Te.

<table>
<thead>
<tr>
<th>Elastic Moduli</th>
<th>Temperature Dependent Elastic Property (GPa) $T = ^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>$42.905 - 7.304 \times 10^{-3} T - 3.249 \times 10^{-6} T^2$</td>
</tr>
<tr>
<td>$E$</td>
<td>$39.669 - 5.481 \times 10^{-2} T - 3.231 \times 10^{-6} T^2$</td>
</tr>
<tr>
<td>$G$</td>
<td>$14.745 - 1.985 \times 10^{-3} T - 1.204 \times 10^{-6} T^2$</td>
</tr>
</tbody>
</table>

6.7 Quasi-Isotropic Wave Propagation

The propagation of high frequency elastic waves (ultrasound) in isotropic polycrystalline bodies is directly related to the (dynamic) elastic moduli of the body. In the long wavelength limit, the longitudinal and shear wave velocities can be expressed in terms of the low frequency limit (static) elastic constants and the density [137]. The longitudinal ($v_l$) and shear ($v_s$) wave velocities were computed from well known relationships

$$v_l = \sqrt{\frac{E}{\rho}} \frac{1-v}{(1+v)(1-2v)},$$  \hspace{1cm} (6.20)

$$v_s = \sqrt{\frac{E}{2\rho}} \frac{1}{1+v} = \sqrt{\frac{G}{\rho}},$$  \hspace{1cm} (6.21)

where $E$ is Young’s modulus, $G$ is the shear modulus, $\rho$ is the density and Poisson’s ratio ($v$) can be expressed as $v = E/2G - 1$. The calculated temperature dependent quasi-isotropic wave velocities (Eqns. (6.20) - (6.21)) are shown in Fig. 6.15. Table 6.4 shows polynomial fits for the temperature dependence of the quasi-isotropic wave velocities of Cd$_{0.96}$Zn$_{0.04}$Te.
Figure 6.15 Temperature dependence quasi-isotropic wave velocities ($v_l$ and $v_s$) for solid $Cd_{0.96}Zn_{0.04}$\(Te\).

Table 6.4: Temperature dependent polynomial fits of the quasi-isotropic wave velocities of $Cd_{0.96}Zn_{0.04}$\(Te\).

<table>
<thead>
<tr>
<th>Type of Wave</th>
<th>Temperature Dependent Wave Velocities (mm/$\mu$s) $T$ = °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_l$</td>
<td>$3.2612 - 2.1161 \times 10^{-4} T - 1.7585 \times 10^{-7} T^2$</td>
</tr>
<tr>
<td>$v_s$</td>
<td>$1.5857 - 8.5394 \times 10^{-4} T - 8.3713 \times 10^{-8} T^2$</td>
</tr>
</tbody>
</table>
6.8 Summary

A laser ultrasonic sensor has been used to determine the ultrasonic TOF and hence velocity of Cd$_{1-y}$Zn$_y$Te with y = 0.04 from 20 to 1140°C. Both the longitudinal and shear waves exhibited a monotonically decreasing velocity with temperature. The solid and liquid exhibited normal semiconducting behavior and did not exhibit any structural changes. When the ingots were heated through the melting point under quasi-equilibrium conditions a ~2 fold decrease was observed in the longitudinal wave velocity, due to the absence of the shear modulus in the liquid phase. These results suggest that the ultrasonic velocity ratio ($v_{\text{sol}}/v_{\text{liq}}$) between the solid and liquid phases is sufficient for the implementation of laser ultrasonic sensors to monitor the liquid-solid interface during vertical Bridgman growth.

The single crystal elastic stiffness constants ($C_{11}$, $C_{12}$ and $C_{44}$) for solid and the adiabatic bulk modulus ($K_s$) for liquid of Cd$_{0.96}$Zn$_{0.04}$Te have been fully evaluated from simple inversion techniques of the temperature dependent ultrasonic velocity in primary $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ orientations and the temperature dependence of the density. The single crystal elastic stiffness constants showed a monotonically decreasing function with increasing temperature in both the solid and liquid phases. In addition, an analysis of the polycrystalline elastic moduli may facilitate evaluation during polycrystalline solidification.
Chapter 7

In-Situ Sensing During Crystal Growth

In the previous chapter, the elastic properties of Cd$_{0.96}$Zn$_{0.04}$Te were fully characterized. These results indicated that under quasi-equilibrium conditions a ~2 fold decrease was observed in the longitudinal wave velocity, due to the absence of the shear modulus in the liquid phase. Thus the ultrasonic velocity ratio ($v_{so}/v_{liq}$)$^1$ between the solid and liquid phases is sufficient for the implementation of the laser ultrasonic sensing methodology, outlined in Chapters 4 and 5, to monitor the melting-solidification characteristics of directionally solidified (Cd,Zn)Te alloys. The incorporation of this laser ultrasonic sensor seeks to gain a better understanding of such growth conditions as melting-solidification characteristics and undercooling effects caused by superheating of the liquid above it's melting point.

---

1. Analogously, the time of flight exhibits a ~2 fold increase upon melting due to the fact that the ultrasonic velocity ($v$) and the time of flight ($\tau$) are directly related through the relationship $v = l/\tau$, where $l$ is a constant propagation distance. Therefore the data presented in this chapter will be presented in terms of the time of flight for a quasi-longitudinal wave.
7.1 Experimental Procedure

7.1.1 Sample Preparation

Cd$_{0.96}$Zn$_{0.04}$Te ingots were supplied by Johnson Matthey Electronics (Spokane, WA). The material consisted of precompounded IRFPA substrate purity polycrystalline equatomic CdTe to which Zn and Te was added to reach the target zinc concentration of 4 at.% ± 1%. The subsequent polycrystalline ingot was then grown from the melt using a commercial 17-zone VB growth furnace. The ingots were encapsulated in 30 mm ID (36 mm OD) quartz ampoules with quartz plugs (to fill in the free volume) and sealed under 10$^{-6}$ torr with a very small free volume to inhibit the vaporization of Cd during subsequent heating, Fig. 7.1. The encapsulated free volume was typically less than 2% of the ingot volume.

![Diagram](image)

**Figure 7.1** A schematic illustration of the Cd$_{0.96}$Zn$_{0.04}$Te ampoule used to monitor the melting-solidification characteristics. (all dimensions in mm).
7.1.2 Laser Ultrasonic Sensing

The ultrasonic time-of-flight's (TOF's) between precisely positioned source and receiver points were measured using the laser ultrasonic system shown in Fig. 7.2. A \~10 ns duration \$Q$-switched Nd:YAG laser pulse of 1.064-\(\mu\)m wavelength was used as the ultrasonic source. The energy per pulse was \~10 mJ and the roughly Gaussian beam of the multimode pulse was focused to an approximate circular spot of 1 mm diameter. Thus, the source power density was \~100 MW/cm\(^2\). The source power density was kept to a minimum as to prevent cracking of the quartz ampoule at high temperature releasing toxic Cd vapor. The quartz ampoule provided a constrained surface resulting in large amplitude longitudinal and shear waves.

The ultrasonic receiver was a Mach-Zehnder heterodyne laser interferometer. It responded to the sample's out-of-plane (normal) surface displacement associated with wavefront arrivals at the receiver point. It was powered by a 5 mW HeNe laser which produced a continuous Gaussian beam of 632.8-nm wavelength focused to a circular spot \~100 \(\mu\)m in diameter. The interferometer had a displacement sensitivity of 0.4 Å/mV and exhibited linear output for displacements up to about 300 Å. For the experiments reported here, maximum surface displacements were on the order of 200 Å. The signal from the interferometer was bandpass filtered between 10 kHz and 10 MHz and recorded with a precision digital oscilloscope at a 2 ns sampling interval using 8-bit analog-to-digital conversion. To improve the signal-to-noise ratio, each waveform used for a TOF measurement was the average of \~10 pulses collected at a pulse repetition rate of 20 Hz. A fast photodiode identified the origination time for the ultrasonic signals.
Figure 7.2. A schematic illustration of the high temperature laser ultrasonic test facility used for monitoring the melting-solidification and directional solidification of (Cd,Zn)Te.
7.1.3 Integrated Growth Furnace

Heating was accomplished with a Thermcraft (Winston-Salem, NC) single zone programmable tubular furnace (1200°C max, 6 in diam). The furnace was equipped with a temperature controller that was able to maintain the temperature to within 1°C. The Cd$_{0.96}$Zn$_{0.04}$Te samples were supported by a AREMCOLOX™ Alumino-Silicate machinable ceramic and quartz support assembly. The laser source and receiver gained access into the furnace through small (~4 mm) slits along the diametral plane of the furnace. The sample temperature was measured with two type R thermocouples affixed to the quartz growth ampoule with tungsten wire. In both cases, the thermocouples were in physical contact with the outer surface of the ampoule. Variations of the temperature in the region of the sample were better than ±2°C.

The z-axis translation stages were controlled using AeroTech Unidex 1 stepper motors. The screw driven translation stages had a movement resolution of 1.27 μm/step with a repeatability of 1.175 μm per 5.08 mm of linear travel and controlled through RS 232C interfaces via a personal computer. Figure 7.3 shows a close up region of the translation stages and ampoule region of the integrated laser ultrasonic growth facility.

7.1.4 Ultrasonic Sensing Strategies

Here, the laser ultrasonic sensor has been fully integrated in the growth furnace. The sensor’s response will be examined for two primary conditions. Firstly, it has been used to monitor the TOF of the melting-solidification characteristics while keeping the furnace stationary and secondly to monitor the TOF during directional solidification of a Cd$_{0.96}$Zn$_{0.04}$Te ingot.
Figure 7.3: A schematic illustration of the translation stages and ampoule region of the integrated laser ultrasonic sensing facility.
7.2 Monitoring The Melting-Solidification of Cd$_{0.96}$Zn$_{0.04}$Te

In this section, the laser ultrasonic sensor has been set up to measure the quasi-longitudinal wave TOF during the melting-solidification of Cd$_{0.96}$Zn$_{0.04}$Te while keeping the furnace stationary. The sample was heated at a rate of 5°C/min up to 1050°C, then heated at a rate of 1°C/min up to 1140°C, held for 15 minutes and cooled along the same path as the heating cycle.

7.2.1 Heating

The experimentally measured quasi-longitudinal wave TOF measured during heating is shown in Fig. 7.4 as a function of process cycle time. Also shown in Fig. 7.4 is the simulated quasi-longitudinal wave TOF. The simulated TOF was calculated assuming the quasi-longitudinal wave propagates with a velocity equivalent to the isotropic polycrystalline average and was calculated from the velocity expressions shown in Table 6.4 and the instantaneous length of Eqn. (6.6). The simulated data, shown for reference purposes, represents the general trend for the quasi-longitudinal wave for which the experimental data may be compared with.

The experimentally measured data shows a gradual increase in the TOF as the sample was heated and a discontinuous increase (~2 fold increase) near the melting point. This discontinuous increase in the quasi-longitudinal wave TOF indicated the beginning of the melting process for the Cd$_{0.96}$Zn$_{0.04}$Te alloy. It can be seen that the change in TOF at the melting point was not instantaneous. There was a slight lag between the experimentally measured TOF and that predicted from the process temperature waveform during the initial melting stages, i.e. melting was observed over a range of temperatures for this process cycle.
It can also be seen from Fig. 7.4 that the quasi-longitudinal wave TOF in the solid phase falls below that predicted for the isotropic polycrystalline average. This behavior is attributed to the fact that the ingots' diameter consisted of ~3 - 5 grain diameters. This was determined visually and not quantitatively characterized. Because the ingots's diameter does not accurately represent a true isotropic polycrystalline average, the simulated quasi-longitudinal wave TOF is shown for comparison purposes only. The data may also be displayed as a function of temperature as shown in Fig. 7.5. The data of Fig. 7.5 shows similar trends to that shown in Fig. 7.4.

To further understand the sluggish melting characteristics observed in Figs. 7.4 and 7.5 it is useful to examine the experimentally observed waveforms for the region near the melting point for this alloy. Figure 7.6 shows the experimental waveforms near the melting point observed during heating. The waveforms of Fig. 7.6(a) - 7.6(g) are shown for temperatures of 1090°C - 1120°C in increments of 5°C. Arrows indicate the quasi-longitudinal wave arrival TOF's in each of the waveforms. Figure 7.6(a) - 7.6(c), 1090°C, 1095°C and 1100°C, respectively, show a waveform indicative of a wave propagating through a solid phase with quasi-longitudinal wave TOF arrivals of ~10μs. Figure 7.6(d) - 7.6(e), 1105°C and 1110°C, respectively, show a waveform indicative of a wave propagating through a partially liquid phase material with quasi-longitudinal wave TOF arrivals of ~20 μs. Where as, Figs. 7.6(f) - 7.6(g), 1115°C and 1120°C, respectively, show a waveform indicative of a wave propagating through a fully liquid phase material with quasi-longitudinal wave TOF arrivals of ~22 μs. The shape and TOF of the waveforms observed in Fig. 7.6 indicate sluggish melting characteristics. It is believed that due to the combination of the low thermal conductivity and high heat capacity for CdTe and its alloys, that melting had begun at ~1100°C and was not fully complete until the process temperature waveform reached was in the range of 1110°C to 1115°C.
Figure 7.4  Time dependent quasi-longitudinal wave TOF measured during the heating portion of the process cycle.

Figure 7.5  Temperature dependent quasi-longitudinal wave TOF measured during the heating portion of the process cycle.
Figure 7.6  Experimental waveforms for the region surrounding the melting point of the Cd$_{0.96}$Zn$_{0.04}$Te alloy observed during heating.
7.2.2 Cooling

The experimentally measured quasi-longitudinal wave TOF monitored during cooling is shown in Fig. 7.7 as a function of process cycle time. Also shown in Fig. 7.7 is the simulated quasi-longitudinal wave TOF. Again, the simulated TOF was calculated from the isotropic polycrystalline elastic constants at the temperature measured from the samples thermocouple. The experimentally measured data shows a gradual decrease of the TOF in the liquid phase as the sample was cooled and exhibited a discontinuous decrease (~2 fold decrease) at a temperature slightly below the melting point of 1098°C. The discontinuous decrease in the quasi-longitudinal wave TOF is indicative of the solidification of the Cd_{0.96}Zn_{0.04}Te ingot. Again the data may also be displayed as a function of temperature as shown in Fig. 7.8 showing similar trends to that of Fig. 7.7.

Unlike during heating of the ingot, the quasi-longitudinal wave TOF exhibited an abrupt decrease at the point of solidification. However, the temperature of the ingot was cooled well below the melting point before solidification was observed with the ultrasonic sensor. Analysis of the waveforms observed during cooling of the Cd_{0.96}Zn_{0.04}Te ingot may prove to be useful and are shown in Fig. 7.9. The waveforms of Fig. 7.9(a) - 7.9(g) are shown for temperatures of 1110°C - 1080°C in increments of 5°C. Again, arrows indicate the quasi-longitudinal wave arrival TOF's in each of the waveforms. Figure 7.9(a) - 7.9(e) exhibit waveforms indicative of wave propagation through a fully liquid phase material with quasi-longitudinal wave arrival TOF's of ~23 - 21 µs, decreasing with temperature. Figure 7.9(f) and 7.9(g) exhibit waveforms indicative of wave propagation through a fully solid phase material with quasi-longitudinal wave arrival TOF's of ~10 µs. This indicates that solidification occurred between 1090°C and 1085°C. Again, it is believed solidification occurred below the equilibrium solidification temperature of 1098°C because of the combination of low thermal conductivity and high heat capacity of
CdTe alloys in addition to constitutional supercooling effects. It has been previously observed that CdTe alloys exhibit constitutional supercooling effects when heated to temperatures greater than 10°C above the melting point [19].

Once the alloy had solidified, it can be seen that the TOF in the solid phase compares well with that predicted by the isotropic polycrystalline elastic moduli (unlike during the heating cycle). This type of behavior is attributed to the fact that the average or effective ingot crystallographic orientation after solidification was different than during the heating cycle and coincidentally better predicted by the elastic moduli for isotropic polycrystalline aggregates. It is interesting to note that in both Figs. 7.7 and 7.8 as the sample was cooled, the experimentally measured quasi-longitudinal wave TOF began to deviate from the predicted TOF at low temperatures (<450°C). It has been previously stated that CdTe and its alloys have low thermal conductivities and high heat capacities, thus it is speculated that the bulk cooling rate of the ingot was slower than the furnace cooling rate and therefore the experimental TOF did not decrease at the same rate as the simulated TOF.
Figure 7.7  Time dependent quasi-longitudinal wave TOF measured during the cooling portion of the process cycle.

Figure 7.8  Temperature dependent quasi-longitudinal wave TOF measured during the cooling portion of the process cycle.
Figure 7.9  Experimental waveforms for the region surrounding the melting point of the Cd$_{0.96}$Zn$_{0.04}$Te alloy observed during cooling.
7.3 Vertical Bridgman Growth of Cd$_{0.96}$Zn$_{0.04}$Te

In this section, the laser ultrasonic sensor has been used to measure the quasi-longitudinal wave TOF to monitor the vertical Bridgman growth characteristics of Cd$_{0.96}$Zn$_{0.04}$Te. Here, investigations have looked at a furnace translation rate of $\sim$1.67 mm/min (i.e. 100 mm/hr). The ingot was heated at a rate of 5°C/min up to 1090°C, then heated at a rate of 1°C/min up to 1140°C, held for 60 min at which point the furnace translation was begun. During the furnace translation segment, the temperature of the single zone furnace was held constant at 1140°C, the insulation zone at the bottom of the furnace provided the necessary cooling to promote directional solidification from the bottom of the ingot towards the top. The ingot’s temperature was taken on the outside of the quartz growth ampoule at the sensor’s level. During the growth runs, the quasi-longitudinal wave TOF’s were measured during the heating and soak segments as well as isothermally during the furnace translation segment of the process cycle.

The experimentally measured quasi-longitudinal wave TOF monitored during the heating and the soak segments of the process cycle are shown in Fig. 7.10. Figure 7.10 also shows the simulated data for the quasi-longitudinal wave TOF. Again the simulated data was calculated assuming isotropic polycrystalline wave propagation for the expressions given in Table 6.4 and the temperature was measured by the ingot’s thermocouples. This simulated data is presented to give the reader a good measure of the ingot’s temperature and also serves as a marker for when melting should occur.
Figure 7.10 Time dependent quasi-longitudinal wave TOF measured during the heating and soak portion of process cycle prior to furnace translation.

The data of Fig. 7.10 shows a gradual increase in the TOF in the solid phase as the ingot was heated, a discontinuous increase near the melting point and a gradual increase in the TOF in the liquid phase. The ingot began melting at ~1100°C and was not fully melted until the temperature reached 1130°C. This can be readily seen by the experimental waveforms displayed in Fig. 7.11. The waveforms of Fig. 7.11(a) - 7.11(g) are shown for temperatures of 1100°C - 1130°C in increments of 5°C. Figure 7.11(a) - 7.11(g) show a gradual change in the shape of the experimental waveforms from a partially melted ingot to a fully melted ingot.
Figure 7.11 Experimental waveforms for the region surrounding the melting point observed during the heating and soak, prior to furnace translation.
After, the ingot was allowed to equilibrate at 1140°C for 60 minutes the furnace translation was begun. The experimentally measured TOF data measured during the soak and subsequent growth cycle are shown in Fig. 7.12. Figure 7.12 shows a relatively constant TOF during the soak, a gradual decrease followed by an abrupt decrease in the TOF as the liquid-solid interface passed through the sensor. The TOF in the liquid state was constant up to ~252 min at which point the TOF began to gradually decrease until ~260 min. This is due to a decrease in the melt’s temperature as the insulation zone approached the sensor. After the insulation zone passed the sensor the liquid-solid interface passed through the sensor and the TOF decreased to ~10 µs. This is also observed in the experimental waveforms of Fig. 7.13. Again the experimental TOF data lagged behind the simulated data and this behavior is believed to be caused by a combination of the low thermal conductivity and high heat capacity of CdTe alloys and supercooling effects.

![Figure 7.12 Time dependent quasi-longitudinal wave TOF measured during the soak and growth portion of the process cycle.](image-url)
Figure 7.13 Experimental observed waveforms for the region surrounding the melting point as the solid-liquid interface passed through the sensor.
7.4 Summary

Here, a laser ultrasonic sensor has been fully integrated into a modified single zone growth furnace. This sensor was developed to examine the potential of laser based ultrasonic sensors to be used for monitoring the solidification characteristics of vertical Bridgman grown Cd$_{0.96}$Zn$_{0.04}$Te. Firstly, it was used to monitor the TOF of the melting-solidification characteristics while keeping the furnace stationary and secondly to monitor the TOF during directional solidification of a Cd$_{0.96}$Zn$_{0.04}$Te ingot.

For the melting-solidification experiment, the experimentally measured quasi-longitudinal wave TOF data exhibited a gradual increase in the TOF as the sample was heated and a discontinuous increase (~2 fold increase) near the melting point. This discontinuous increase in the quasi-longitudinal wave TOF indicated the beginning of the melting process for the Cd$_{0.96}$Zn$_{0.04}$Te alloy. The data indicated sluggish melting characteristics as the alloy was not fully molten until the reference thermocouple temperature was 1115°C. The experimentally measured data also exhibited a gradual decrease in the TOF as the sample was cooled and a discontinuous decrease (~2 fold decrease) at a temperature of 1085°C. The discontinuous decrease in the quasi-longitudinal wave TOF indicated solidification of the Cd$_{0.96}$Zn$_{0.04}$Te ingot. However, the temperature of the ingot was cooled well below the melting point before solidification was observed with the ultrasonic sensor, indicating that solidification occurred abruptly between 1090°C and 1085°C. This behavior is believed to be caused by a combination of the low thermal conductivity and the high heat capacity of this alloy in addition to constitutional supercooling effects. It has been previously observed that CdTe alloys exhibit constitutional supercooling effects when heated to temperatures greater than 10°C above the melting point [19] and this sluggish melting behavior was previously observed with an eddy current sensing system [72].
During directional solidification, the laser ultrasonic TOF data exhibited a gradual increase in the TOF in the solid phase as the ingot was heated, a discontinuous increase near the melting point and a gradual increase in the TOF in the liquid phase indicating the ingot began melting at ~1100°C and was not fully melted until the temperature reached 1120°C. During directional solidification the experimentally measured quasi-longitudinal wave TOF data collected during the soak and subsequent growth cycle exhibited a relatively constant TOF in the liquid state followed by an abrupt decrease in the TOF as the solid-liquid interface passed through the sensor. The TOF in the liquid state was constant up to ~252 min at which point the TOF began to gradually decrease until ~260 min. The decrease in the quasi-longitudinal wave TOF is due to a decrease in the melt’s temperature as the insulation zone approached the sensor. As the start of the insulation zone passed the sensor the liquid-solid interface passed through the sensor and the quasi-longitudinal wave TOF decreased to ~10 μs indicating the passage of the liquid-solid interface.
Chapter 8

Discussion

The many difficulties associated with the growth of premium quality CdTe and (Cd,Zn)Te alloys has stimulated an interest in the development of non-invasive approaches to monitor critical growth parameters such as the solid-liquid interface position and shape during VB growth. Here, an ultrasonic transmission based approach has been investigated. The sensors development is based upon the recognition that in most materials, the ultrasonic velocity (and the elastic stiffness constants that control it) of the solid and liquid phases are temperature dependent and an abrupt increase of the longitudinal wave velocity occurs upon solidification.

This abrupt velocity increase upon solidification, will therefore cause the time-of-flight (TOF) of ultrasonic pulses that propagate through a sample to increase when it melts. Ultrasonic rays that propagate through the interface region during solidification are therefore likely to be sensitive to the instantaneous position and shape of the solid-liquid interface. Therefore, the measurement of the time-of-flight for sets of ultrasonic rays that traverse the region, combined with reconstruction algorithms, have stimulated interest to
determine critical growth parameters such as the solid-liquid interface position, interface shape and local velocity fields (which are related to local thermal gradients).

A laser ultrasonic sensor has been used to determine the ultrasonic TOF and hence velocity of Cd$_{0.96}$Zn$_{0.04}$Te from 20 to 1140°C, encompassing the range of temperatures typically encountered during growth of CdTe and its (Cd,Zn)Te substitutional solid solution alloys. When this alloy was heated through the melting point under quasi-equilibrium conditions a ~2 fold decrease was observed in the longitudinal wave velocity, due to the absence of the shear modulus in the liquid phase. These results suggest that the ultrasonic velocity ratio ($v_{sol}/v_{liq}$) between the solid and liquid phases are sufficient for the implementation of laser ultrasonic sensors to monitor the liquid-solid interface during vertical Bridgman growth.

Due to the fact that ray propagation in partially solidified bodies is complex and defines the sensing methodology, extensive numerical simulations of 2-D [138] (diametral and transverse planes) and 3-D [139] wave propagation in anisotropic cylindrical single crystal solid-liquid bodies where the receiver is positioned at arbitrary locations relative to the source have been conducted to evaluate the potential use of laser ultrasonic TOF data during VB growth of single crystal semiconductors. It was shown that in many cases, 3-D wave propagation behavior in single crystal solid-liquid bodies can be interpreted via the 2-D wave propagation behavior in diametral and transverse planes. Also, ultrasonic sensing in the diametral plane is the preferred sensing configuration because the plane in which rays propagate (the diametral plane) is known a priori and a large number of rays with different acoustical properties (i.e. singly and doubly transmitted rays) are available in this plane for interface reconstruction. Rays propagating in non diametral planes can also be used for interface sensing. However, the plane in which reflected and transmitted rays propagate is not known beforehand and needs to be determined at each intersection.
point of the ray path with the interface and fewer rays are available for interface reconstruction on these non diametral planes [140,141].

To aid in the sensors development, a bench top laser ultrasonic system has been developed to measure TOF projection data of rays penetrating model isotropic solid-liquid interface configurations. A combination of ray path, TOF and wavefront analysis was used to fully characterize potential diametral plane sensing configurations for three interface shapes (convex, planar and concave). These experiments indicated that fan-beam TOF projection data sets collected in the diametral plane reveals significant information about the solid-liquid interface’s position and interface height. In addition, a nonlinear least-squares reconstruction algorithm was developed to quantitatively recover the solid-liquid interface position, the interface height and the local velocity fields in the solid and liquid phases.

A laser ultrasonic sensor has been fully integrated into a modified single zone growth furnace. This sensor was developed to examine the potential of laser based ultrasonic sensors to be used for monitoring the solidification characteristics of vertical Bridgman grown Cd$_{0.96}$Zn$_{0.04}$Te. It was used to monitor the TOF of the melting-solidification characteristics while keeping the furnace stationary and to monitor the TOF during directional solidification of a Cd$_{0.96}$Zn$_{0.04}$Te ingot.

For the melting-solidification experiment, the experimentally measured quasi-longitudinal wave TOF data exhibited a gradual increase in the TOF as the sample was heated and a discontinuous increase (~2 fold increase) near the melting point. This discontinuous increase in the quasi-longitudinal wave TOF indicated the beginning of the melting process for the Cd$_{0.96}$Zn$_{0.04}$Te alloy. The data indicated sluggish melting characteristics as the alloy was not fully molten until the reference thermocouple temperature was 1115°C. The experimentally measured data also exhibited a gradual decrease in the TOF as the
sample was cooled and a discontinuous decrease (≈2 fold decrease) at a temperature of 1085°C. The discontinuous decrease in the quasi-longitudinal wave TOF indicated solidification of the Cd$_{0.96}$Zn$_{0.04}$Te ingot. However, the temperature of the ingot was cooled well below the melting point before solidification was observed with the ultrasonic sensor, indicating that solidification occurred abruptly between 1090°C and 1085°C. This behavior is believed to be caused by a combination of the low thermal conductivity and the high heat capacity of this alloy in addition to constitutional supercooling effects. It has been previously observed that CdTe alloys exhibit constitutional supercooling effects when heated to temperatures greater than 10°C above the melting point [19] and this sluggish melting behavior was previously observed with an eddy current sensing system [72].

During directional solidification, the laser ultrasonic TOF data exhibited a gradual increase in the TOF in the solid phase as the ingot was heated, a discontinuous increase near the melting point and a gradual increase in the TOF in the liquid phase indicating the ingot began melting at ≈1100°C and was not fully melted until the temperature reached 1120°C. During directional solidification the experimentally measured quasi-longitudinal wave TOF data collected during the soak and subsequent growth cycle exhibited a relatively constant TOF in the liquid state followed by an abrupt decrease in the TOF as the solid-liquid interface passed through the sensor.

Therefore, this laser ultrasonic sensor has been successfully developed and used to monitor the melting and solidification characteristics of a Cd$_{0.96}$Zn$_{0.04}$Te ingot. However, experimental complications prevented the use of this sensor to determine the liquid-solid interface shape and position during directional solidification. The following will address these limitations and recommend new laser based sensing methodologies which are more robust and better suited for on-line process control of industrial based applications.
As stated in Chapter 3, the optical detection of ultrasound can be accomplished interferometrically by collecting the light reflected (or scattered) from a surface as it is subjected to an ultrasonic disturbance. Surface displacement interferometers interfere the scattered/reflected light, which produces a speckle pattern, with a reference beam resulting in a measurement of the optical phase which is directly related to the instantaneous surface displacement. Most optical ultrasonic detection systems are based on surface displacement interferometers such as the Michelson or Mach-Zehnder type interferometer. The Mach-Zehnder heterodyne interferometer (as used here) uses a two beam system in which a single laser beam is split and frequency shifted (via a Bragg cell).

These Michelson and Mach-Zehnder type interferometers have not achieved their ultimate potential in the manufacturing environment because of two main difficulties [142-148]. Firstly, low-frequency large-amplitude phase fluctuations created by ambient vibrations can bias conventional interferometric receivers out of quadrature, reducing their sensitivity. Secondly, multiple speckles produced when laser beams reflect from rough or diffuse surfaces can wash out the ultrasonic signal or significantly reduce the signal-to-noise ratio through phase mixing. Therefore, Michelson and Mach-Zehnder type interferometers have proven well suited for laboratory operation on vibration free tables when used on smooth, near optically flat samples which minimize the speckle reflectance [112, 142-148].

It has been visually observed that during the Cd$_{0.96}$Zn$_{0.04}$Te growth runs, the speckle pattern produced from the Mach-Zehnder interferometer varied in both intensity and spacial variability due to ambient vibrations. This resulted in the need for periodic realignment of the interferometer to increase the signal-to-noise ratio, thus impeding the robustness of the sensor over long periods of time.
In recent years, there has been considerable improvement in laser ultrasonic interferometers. These interferometers reduce the problem of speckle motion by incorporating an adaptive photodetector based on a nonsteady state photo-induced electro motive force (emf) [142-148]. This sensor generates a time-varying output current which is proportional to the ultrasonic surface displacement and can be used on rough surfaces and moving parts, suiting them well for industrial applications such as crystal growth furnaces.

The laser ultrasonic approach exhibits potential for providing critical growth information during the vertical Bridgman growth process. The sensing methodologies outline here integrated into vertical Bridgman growth furnaces with robust laser interferometers could provide useful information to the crystal grower in efforts to obtain higher yields of high quality semiconductors. It is believed that due to the fact that laser ultrasonic sensors may provide "real time" data, they offer the possibility of new sensor based process control technologies for in-situ monitoring and direct feedback control of vertical Bridgman growth technologies.
Chapter 9

Conclusions

The difference in the ultrasonic velocity of a longitudinal wave propagating in solid and liquid (Cd,Zn)Te has led to an interest in the use of ultrasonic time-of-flight (TOF) measurements as a potential non invasive sensing methodology to monitor the solid-liquid interface during vertical Bridgman crystal growth provided, the temperature dependence of the ultrasonic velocities (which depend on the elastic stiffness constant and the density) for both the solid and the liquid phases are known a priori.

A combination of ray tracing, wavefront and TOF analysis and experimental testing on model cylindrical solid-liquid interfaces with a laser ultrasonic system was used to develop sensing concepts to determine a solid-liquid interface’s location, curvature and velocity fields from ultrasonic TOF projection data collected in the diametral plane. Because convex, planar and concave solid-liquid interfaces resulted in uniquely different TOF data profiles, the interface shape was readily determined from the TOF data. When the TOF data collected in the diametral plane was used in conjunction with a nonlinear least squares reconstruction algorithm, the interface geometry (i.e. location and curvature)
was successfully reconstructed and the ultrasonic velocities of both solid and liquid obtained.

Prior to the sensor’s integration into a crystal growth furnace, the laser ultrasonic sensor was used to measure the ultrasonic TOF and calculate the elastic stiffness constants of Cd$_{1-y}$Zn$_y$Te with $y = 0.04$ from 20 to 1140°C. The single crystal elastic stiffness constants ($C_{11}$, $C_{12}$ and $C_{44}$) for solid and the adiabatic bulk modulus ($K_S$) for liquid of Cd$_{0.96}$Zn$_{0.04}$Te have been fully evaluated from simple inversion techniques of the temperature dependent ultrasonic velocity in primary $(100)$, $(110)$ and $(111)$ orientations and the temperature dependence of the density. The elastic stiffness constants showed a monotonically decreasing function with increasing temperature in both the solid and liquid phases.

The longitudinal and shear waves exhibited a monotonically decreasing velocity with temperature. The solid and liquid exhibited normal semiconducting behavior and did not exhibit any structural changes. When the alloy was heated through the melting point under quasi-equilibrium conditions a $\sim$2 fold decrease was observed in the longitudinal wave velocity, due to the absence of the shear modulus in the liquid phase. These results suggest that the ultrasonic velocity ratio ($\nu_s/\nu_l$) between the solid and liquid phases are sufficient for the implementation of this sensing technology to monitor the liquid-solid interface during vertical Bridgman growth.

The laser ultrasonic sensor was fully integrated into a modified single zone growth furnace. This sensor was developed to examine the potential of laser based ultrasonic sensors to be used for monitoring the solidification characteristics of vertical Bridgman grown Cd$_{0.96}$Zn$_{0.04}$Te. Firstly, it was used to monitor the TOF of the melting-solidification characteristics while keeping the furnace stationary and secondly to monitor the TOF during directional solidification of a Cd$_{0.96}$Zn$_{0.04}$Te ingot.
For the melting-solidification experiment, the experimentally measured quasi-longitudinal wave TOF data exhibited a gradual increase in the TOF as the sample was heated and a discontinuous increase (~2 fold increase) near the melting point. This discontinuous increase in the quasi-longitudinal wave TOF indicated the beginning of the melting process for the Cd$_{0.96}$Zn$_{0.04}$Te alloy. The data indicated sluggish melting characteristics as the alloy was not fully molten until the reference thermocouple temperature was 1115°C. The experimentally measured data also exhibited a gradual decrease in the TOF as the sample was cooled and a discontinuous decrease (~2 fold decrease) at a temperature of 1085°C. The discontinuous decrease in the quasi-longitudinal wave TOF indicated solidification of the Cd$_{0.96}$Zn$_{0.04}$Te ingot. However, the temperature of the ingot was cooled well below the melting point before solidification was observed with the ultrasonic sensor, indicating that solidification occurred abruptly between 1090°C and 1085°C. This behavior is believed to be caused by a combination of the low thermal conductivity and the high heat capacity of this alloy in addition to constitutional supercooling effects.

During directional solidification, the laser ultrasonic TOF data exhibited a gradual increase in the TOF in the solid phase as the ingot was heated, a discontinuous increase near the melting point and a gradual increase in the TOF in the liquid phase indicating the ingot began melting at ~1100°C and was not fully melted until the temperature reached 1120°C. During directional solidification, the experimentally measured quasi-longitudinal wave TOF data collected during the soak and subsequent growth cycle exhibited a relatively constant TOF in the liquid state followed by an abrupt decrease in the TOF as the solid-liquid interface passed through the sensor. The TOF in the liquid state was constant up to ~252 minutes at which point the TOF began to gradually decrease until ~260 minutes. The decrease in TOF was due to a decrease in the melt's temperature as the insulation zone approached the sensor. As the start of the insulation zone passed the sensor, the solid-
liquid interface passed through the sensor and the quasi-longitudinal wave TOF decreased to ~10 μs.

A novel laser ultrasonic sensor was successfully developed to monitor the melting-solidification characteristics and the liquid-solid interface during directional solidification of Cd$_{0.96}$Zn$_{0.04}$Te. Due to the fact that ultrasonic sensors may provide "real time" data, it offers the possibility of new sensor based process control technologies for in-situ monitoring and direct feedback control of vertical Bridgman growth technologies.
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Appendix A

The following algorithm was developed to calculate 2-dimensional slowness, phase and group velocity surfaces for any crystal system. The input parameters are the stiffness matrix, density and two orthogonal direction for the velocity surface. The subroutines used are from the SLATEC Common Mathematical Library which is an extensive public-domain FORTRAN source code library (consisting of more than 1400 routines and 300,000 lines of code and documentation) developed and maintained by a consortium of the Department of Energy and the Department of Defense laboratories. Version 4.0 of the library was released in December of 1992. The SLATEC gopher tree is accessible from the Numerical Recipes Software information tree at http:\\gopher.cfata9.harvard.edu.

Subroutines located within:

- RS - Computes eigenvalues and eigenvectors of real symmetric (complete Hermitian) matrix.
- TQL2 - Computes eigenvalues and eigenvectors of symmetric tridiagonal matrix by QL method.
- TQLRAT - Computes eigenvalues of symmetric tridiagonal matrix a rational variant of the QL method.
- TRED1 - Reduces real symmetric matrix to symmetric tridiagonal matrix using orthogonal similarity transformations.
- TRED2 - Reduces real symmetric matrix to symmetric tridiagonal matrix using and accumulating orthogonal transformations.
program velocc
*
   dimension stiff(6,6),abscissa(3),ordinate(3)
   dimension vnorm(3),rot(3,3),ss(3),divmat(3,6),gradmat(6,3)
   dimension dir(3),absunit(3),ordunit(3),veloc(361,6),slow(361,6)
   dimension tempmat(6,3),chris(3,3),w(3,3),z(3,3),fv1(3),fv2(3)
   dimension polarql(3),polarsl(3),polars2(3),grpvel(3),group(361,6)
   dimension dirql(1),dirs1(3),dirs2(3)
   integer nm,n,matz,lerr
*
   open(50,file='cdtell1.dat')
   open(60,file='cdtelllp.dat')
   open(61,file='cdtell1s.dat')
   open(62,file='cdtelllg.dat')
*
   n = 3
   nm = 3
   matz = 1
   pi = acos(-1.)
   dtr = pi/180.
*
   do 2 i = 1,6
      read(50,*) stiff(i,1),stiff(i,2),stiff(i,3),
          -              stiff(i,4),stiff(i,5),stiff(i,6)
   2 continue
*
   write(6,*) ('Stiffness Matrix - Silicon (GPa)')
   write(6,*)
   do 3 i = 1,6
      write(6,501) stiff(i,1),stiff(i,2),stiff(i,3),
          -              stiff(i,4),stiff(i,5),stiff(i,6)
   3 continue
   501 format(6f7.2)
   write(6,*)
*
   read(50,*) density
   write(6,*) 'density: ',density,' (gm/cm3)'
*
   read(50,*) abscissa(1),abscissa(2),abscissa(3)
   write(6,*)
   write(6,503) abscissa(1),abscissa(2),abscissa(3)
   503 format('abscissa: ',3f4.1)
*
   read(50,*) ordinate(1),ordinate(2),ordinate(3)
   write(6,*)
   write(6,504) ordinate(1),ordinate(2),ordinate(3)
   write(6,*)
   504 format('ordinate: ',3f4.1)
*
   absn = sqrt(abscissa(1)*abscissa(1) +
          -              abscissa(2)*abscissa(2) +
- \quad \text{abscissa}(3) * \text{abscissa}(3) \\
- \quad \text{ordinate}(1) * \text{ordinate}(1) + \\
- \quad \text{ordinate}(2) * \text{ordinate}(2) + \\
- \quad \text{ordinate}(3) * \text{ordinate}(3) \\
* \quad \text{write}(6,*), \text{abscissa}, \text{magnitude: '),}, \text{absn} \\
\quad \text{write}(6,*), \text{ordinate}, \text{magnitude: '),}, \text{ordn} \\
\quad \text{write}(6,*), \text{abscissa}(1)/\text{absn} \\
\quad \text{absunit}(2) = \text{abscissa}(2)/\text{absn} \\
\quad \text{absunit}(3) = \text{abscissa}(3)/\text{absn} \\
* \quad \text{write}(6,505), \text{absunit}(1), \text{absunit}(2), \text{absunit}(3) \\
\quad \text{write}(6,*), \text{3f4.1} \\
* \quad \text{ordunit}(1) = \text{ordinate}(1)/\text{ordn} \\
\quad \text{ordunit}(2) = \text{ordinate}(2)/\text{ordn} \\
\quad \text{ordunit}(3) = \text{ordinate}(3)/\text{ordn} \\
* \quad \text{write}(6,506), \text{ordunit}(1), \text{ordunit}(2), \text{ordunit}(3) \\
\quad \text{write}(6,*), \text{3f4.1} \\
* \quad \text{vnorm}(1) = \text{absunit}(2) * \text{ordunit}(3) - \text{absunit}(3) * \text{ordunit}(2) \\
\quad \text{vnorm}(2) = \text{absunit}(3) * \text{ordunit}(1) - \text{absunit}(1) * \text{ordunit}(3) \\
\quad \text{vnorm}(3) = \text{absunit}(1) * \text{ordunit}(2) - \text{absunit}(2) * \text{ordunit}(1) \\
* \quad \text{write}(6,507), \text{vnorm}(1), \text{vnorm}(2), \text{vnorm}(3) \\
* \quad \text{write}(6,*), \text{3f4.1} \\
* \quad \text{rot}(1,1) = \text{absunit}(1) \\
\quad \text{rot}(1,2) = \text{absunit}(2) \\
\quad \text{rot}(1,3) = \text{absunit}(3) \\
\quad \text{rot}(2,1) = \text{ordunit}(1) \\
\quad \text{rot}(2,2) = \text{ordunit}(2) \\
\quad \text{rot}(2,3) = \text{ordunit}(3) \\
\quad \text{rot}(3,1) = \text{vnorm}(1) \\
\quad \text{rot}(3,2) = \text{vnorm}(2) \\
\quad \text{rot}(3,3) = \text{vnorm}(3) \\
* \quad \text{do} \ 4 \ \text{ang} = 1,361 \\
* \quad \quad \text{ss}(1) = \cos(\text{ang}*\text{dtr}) \\
\quad \quad \text{ss}(2) = \sin(\text{ang}*\text{dtr}) \\
\quad \quad \text{ss}(3) = 0. \\
*
dir(1) = ss(1)*rot(1,1) + ss(2)*rot(2,1) + ss(3)*rot(3,1)
dir(2) = ss(1)*rot(1,2) + ss(2)*rot(2,2) + ss(3)*rot(3,2)
dir(3) = ss(1)*rot(1,3) + ss(2)*rot(2,3) + ss(3)*rot(3,3)

* 
divmat(1,1) = dir(1)
divmat(1,2) = 0.
divmat(1,3) = 0.
divmat(1,4) = 0.
divmat(1,5) = dir(3)
divmat(1,6) = dir(2)
divmat(2,1) = 0.
divmat(2,2) = dir(2)
divmat(2,3) = 0.
divmat(2,4) = dir(3)
divmat(2,5) = 0.
divmat(2,6) = dir(1)
divmat(3,1) = 0.
divmat(3,2) = 0.
divmat(3,3) = dir(3)
divmat(3,4) = dir(2)
divmat(3,5) = dir(1)
divmat(3,6) = 0.

* 
do 5 i = 1,3
   do 6 j = 1,6
      gradmat(j,i) = divmat(i,j)
   6 continue
   5 continue

* 
do 7 i = 1,6
   do 8 j = 1,3
      temp = 0.
      do 9 k = 1,6
         temp = temp + stiff(i,k)*gradmat(k,j)
      9 continue
      tempmat(i,j) = temp
   8 continue
   7 continue

* 
do 10 i = 1,3
   do 11 j = 1,3
      temp = 0.
      do 12 k = 1,6
         temp = temp + divmat(i,k)*tempmat(k,j)
      12 continue
      chris(i,j) = temp
   11 continue
   10 continue

* 
write(75,*) chris(1,1),chris(1,2),chris(1,3)
* write(75,*) chris(2,1),chris(2,2),chris(2,3)
* write (75, *) chris (3, 1), chris (3, 2), chris (3, 3)
* write (75, *)
*
call rs (nm, n, chris, w, matz, z, fvl, fvl, ierr)
*
* qlong = sqrt (w (3) / density)
qshear1 = sqrt (w (2) / density)
qshear2 = sqrt (w (1) / density)
*
slong = 1. / qlong
sshear1 = 1. / qshear1
sshear2 = 1. / qshear2
*
veloc (ang, 1) = qlong * cos (ang * dtr)
veloc (ang, 2) = qlong * sin (ang * dtr)
veloc (ang, 3) = qshear1 * cos (ang * dtr)
veloc (ang, 4) = qshear1 * sin (ang * dtr)
veloc (ang, 5) = qshear2 * cos (ang * dtr)
veloc (ang, 6) = qshear2 * sin (ang * dtr)
*
slow (ang, 1) = slong * cos (ang * dtr)
slow (ang, 2) = slong * sin (ang * dtr)
slow (ang, 3) = sshear1 * cos (ang * dtr)
slow (ang, 4) = sshear1 * sin (ang * dtr)
slow (ang, 5) = sshear2 * cos (ang * dtr)
slow (ang, 6) = sshear2 * sin (ang * dtr)
*
polarql (1) = z (1, 3)
polarql (2) = z (2, 3)
polarql (3) = z (3, 3)
*
polarls (1) = z (1, 2)
polarls (2) = z (2, 2)
polarls (3) = z (3, 2)
*
polars (1) = z (1, 1)
polars (2) = z (2, 1)
polars (3) = z (3, 1)
*
taefvqlx = dir (1) * polarql (1) ** 2 * stiff (1, 1) +
  - polarql (1) * stiff (1, 2) *
- (dir (2) * polarql (2) + dir (3) * polarql (3)) +
- stiff (4, 4) *
- (polarql (2) *
- (dir (2) * polarql (1) + dir (1) * polarql (2)) +
- polarql (3) *
- (dir (3) * polarql (1) + dir (1) * polarql (3)))
*
taefvqly = dir (2) * polarql (2) ** 2 * stiff (1, 1) +
  - polarql (2) * stiff (1, 2) *
\[
\begin{align*}
\text{taefvqlz} &= \text{dir}(3) \cdot \text{polarql}(3) \cdot 2 \cdot \text{stiff}(1,1) + \\
& \quad \text{polarql}(3) \cdot \text{stiff}(1,2) + \\
& \quad \text{dir}(1) \cdot \text{polarql}(1) + \text{dir}(2) \cdot \text{polarql}(2) + \\
& \quad \text{stiff}(4,4) + \\
& \quad \text{polarql}(1) + \\
& \quad \text{dir}(1) \cdot \text{polarql}(3) + \text{dir}(3) \cdot \text{polarql}(1) + \\
& \quad \text{polarql}(2) + \\
& \quad \text{dir}(2) \cdot \text{polarql}(3) + \text{dir}(3) \cdot \text{polarql}(2))
\end{align*}
\]

\[
\begin{align*}
\text{taefvqlt} &= \sqrt{\text{taefvqlx}^2 + \text{taefvqly}^2 + \text{taefvqlz}^2}
\end{align*}
\]

\[
\begin{align*}
\text{dirql}(1) &= \frac{\text{taefvqlx}}{\text{taefvqlt}} \\
\text{dirql}(2) &= \frac{\text{taefvqly}}{\text{taefvqlt}} \\
\text{dirql}(3) &= \frac{\text{taefvqlz}}{\text{taefvqlt}}
\end{align*}
\]

\[
\begin{align*}
\text{pftempql} &= \cos(\text{dir}(1) \cdot \text{dirql}(1) + \\
& \quad \text{dir}(2) \cdot \text{dirql}(2) + \\
& \quad \text{dir}(3) \cdot \text{dirql}(3))
\end{align*}
\]

\[
\begin{align*}
\text{taefvslx} &= \text{dir}(1) \cdot \text{polarsl}(1) \cdot 2 \cdot \text{stiff}(1,1) + \\
& \quad \text{polarsl}(1) \cdot \text{stiff}(1,2) + \\
& \quad \text{dir}(2) \cdot \text{polarsl}(2) + \text{dir}(3) \cdot \text{polarsl}(3) + \\
& \quad \text{stiff}(4,4) + \\
& \quad \text{polarsl}(2) + \\
& \quad \text{dir}(2) \cdot \text{polarsl}(1) + \text{dir}(1) \cdot \text{polarsl}(2) + \\
& \quad \text{polarsl}(3) + \\
& \quad \text{dir}(3) \cdot \text{polarsl}(1) + \text{dir}(1) \cdot \text{polarsl}(3))
\end{align*}
\]

\[
\begin{align*}
\text{taefvslly} &= \text{dir}(2) \cdot \text{polarsl}(2) \cdot 2 \cdot \text{stiff}(1,1) + \\
& \quad \text{polarsl}(2) \cdot \text{stiff}(1,2) + \\
& \quad \text{dir}(3) \cdot \text{polarsl}(3) + \text{dir}(1) \cdot \text{polarsl}(1) + \\
& \quad \text{stiff}(4,4) + \\
& \quad \text{polarsl}(3) + \\
& \quad \text{dir}(3) \cdot \text{polarsl}(2) + \text{dir}(2) \cdot \text{polarsl}(3) + \\
& \quad \text{polarsl}(1) + \\
& \quad \text{dir}(1) \cdot \text{polarsl}(2) + \text{dir}(2) \cdot \text{polarsl}(1))
\end{align*}
\]

\[
\begin{align*}
\text{taefvslz} &= \text{dir}(3) \cdot \text{polarsl}(3) \cdot 2 \cdot \text{stiff}(1,1) + \\
& \quad \text{polarsl}(3) \cdot \text{stiff}(1,2) + \\
& \quad \text{dir}(1) \cdot \text{polarsl}(1) + \text{dir}(2) \cdot \text{polarsl}(2) + \\
& \quad \text{stiff}(4,4) + \\
& \quad \text{polarsl}(1) + \\
& \quad \text{dir}(1) \cdot \text{polarsl}(3) + \text{dir}(3) \cdot \text{polarsl}(1) + \\
& \quad \text{polarsl}(2)
\end{align*}
\]
- \( (\text{dir}(2) \cdot \text{polars1}(3) + \text{dir}(3) \cdot \text{polars1}(2)) \)

* \( \text{taefvs1t} = \sqrt{\text{taefvs1x}^2 + \text{taefvs1y}^2 + \text{taefvs1z}^2} \)

* \( \text{dirs1}(1) = \text{taefvs1x}/\text{taefvs1t} \)
* \( \text{dirs1}(2) = \text{taefvs1y}/\text{taefvs1t} \)
* \( \text{dirs1}(3) = \text{taefvs1z}/\text{taefvs1t} \)

* \( \text{pftemps1} = \cos(\text{dir}(1) \cdot \text{dirs1}(1) + \)
  \- \text{dir}(2) \cdot \text{dirs1}(2) + \)
  \- \text{dir}(3) \cdot \text{dirs1}(3)) \)

* \( \text{taefvs2x} = \text{dir}(1) \cdot \text{polars2}(1)^2 \cdot \text{stiff}(1,1) + \)
  \- \text{polars2}(1) \cdot \text{stiff}(1,2) \cdot \)
  \- (\text{dir}(2) \cdot \text{polars2}(2) + \text{dir}(3) \cdot \text{polars2}(3)) + \)
  \- \text{stiff}(4,4) \cdot \)
  \- \text{polars2}(2) \cdot \)
  \- (\text{dir}(2) \cdot \text{polars2}(1) + \text{dir}(1) \cdot \text{polars2}(2)) + \)
  \- \text{polars2}(3) \cdot \)
  \- (\text{dir}(3) \cdot \text{polars2}(1) + \text{dir}(1) \cdot \text{polars2}(3)) \)

* \( \text{taefvs2y} = \text{dir}(2) \cdot \text{polars2}(2)^2 \cdot \text{stiff}(1,1) + \)
  \- \text{polars2}(2) \cdot \text{stiff}(1,2) \cdot \)
  \- (\text{dir}(3) \cdot \text{polars2}(3) + \text{dir}(1) \cdot \text{polars2}(1)) + \)
  \- \text{stiff}(4,4) \cdot \)
  \- \text{polars2}(3) \cdot \)
  \- (\text{dir}(3) \cdot \text{polars2}(2) + \text{dir}(2) \cdot \text{polars2}(3)) + \)
  \- \text{polars2}(1) \cdot \)
  \- (\text{dir}(1) \cdot \text{polars2}(2) + \text{dir}(2) \cdot \text{polars2}(1)) \)

* \( \text{taefvs2z} = \text{dir}(3) \cdot \text{polars2}(3)^2 \cdot \text{stiff}(1,1) + \)
  \- \text{polars2}(3) \cdot \text{stiff}(1,2) \cdot \)
  \- (\text{dir}(1) \cdot \text{polars2}(1) + \text{dir}(2) \cdot \text{polars2}(2)) + \)
  \- \text{stiff}(4,4) \cdot \)
  \- \text{polars2}(1) \cdot \)
  \- (\text{dir}(1) \cdot \text{polars2}(3) + \text{dir}(3) \cdot \text{polars2}(1)) + \)
  \- \text{polars2}(2) \cdot \)
  \- (\text{dir}(2) \cdot \text{polars2}(3) + \text{dir}(3) \cdot \text{polars2}(2)) \)

* \( \text{taefvs2t} = \sqrt{\text{taefvs2x}^2 + \text{taefvs2y}^2 + \text{taefvs2z}^2} \)

* \( \text{dirs2}(1) = \text{taefvs2x}/\text{taefvs2t} \)
* \( \text{dirs2}(2) = \text{taefvs2y}/\text{taefvs2t} \)
* \( \text{dirs2}(3) = \text{taefvs2z}/\text{taefvs2t} \)

* \( \text{pftemps2} = \cos(\text{dir}(1) \cdot \text{dirs2}(1) + \)
  \- \text{dir}(2) \cdot \text{dirs2}(2) + \)
  \- \text{dir}(3) \cdot \text{dirs2}(3)) \)

\( \text{grpvel}(1) = \text{qlong}/\cos(\text{pftemps1}) \)
\( \text{grpvel}(2) = \text{qshear1}/\cos(\text{pftemps1}) \)
\[ \text{group}(\text{ang,1}) = \frac{\text{grpvel}(1) \times \sqrt{6.}}{6.*} \]
- \( \text{dirql}(1) + \text{dirql}(2) - 2 \times \text{dirql}(3) \)
\[ \text{group}(\text{ang,2}) = \frac{\text{grpvel}(1) \times \sqrt{2.}}{2.*} \]
- \( -\text{dirql}(1) + \text{dirql}(2) \)
\[ \text{group}(\text{ang,3}) = \frac{\text{grpvel}(2) \times \sqrt{6.}}{6.*} \]
- \( \text{dirs1}(1) + \text{dirs1}(2) - 2 \times \text{dirs1}(3) \)
\[ \text{group}(\text{ang,4}) = \frac{\text{grpvel}(2) \times \sqrt{2.}}{2.*} \]
- \( \text{dirs1}(1) + \text{dirs1}(2) \)
\[ \text{group}(\text{ang,5}) = \frac{\text{grpvel}(3) \times \sqrt{6.}}{6.*} \]
- \( \text{dirs2}(1) + \text{dirs2}(2) - 2 \times \text{dirs2}(3) \)
\[ \text{group}(\text{ang,6}) = \frac{\text{grpvel}(3) \times \sqrt{2.}}{2.*} \]
- \( \text{dirs2}(1) + \text{dirs2}(2) \)

4 continue

\[
\begin{align*}
\text{do} & 14 \ i = 1,361 \\
\text{write}(60,550) & \text{veloc}(i,1),\text{veloc}(i,2),\text{veloc}(i,3), \\
& \text{veloc}(i,4),\text{veloc}(i,5),\text{veloc}(i,6) \\
\text{write}(61,550) & \text{slow}(i,1),\text{slow}(i,2),\text{slow}(i,3), \\
& \text{slow}(i,4),\text{slow}(i,5),\text{slow}(i,6) \\
\text{write}(62,550) & \text{group}(i,1),\text{group}(i,2),\text{group}(i,3), \\
& \text{group}(i,4),\text{group}(i,5),\text{group}(i,6) \\
\end{align*}
\]

14 continue

550 format(7f10.3)

stop
end

subroutine rs(nm,n,a,w,matz,z,fv1,fv2,ierr)

integer n,nm,ierr,matz
real a(nm,n),w(n),z(nm,n),fv1(n),fv2(n)

***first executable statement rs
if (n .le. nm) go to 10
ierr = 10 * n
go to 50

10 if (matz .ne. 0) go to 20

............ find eigenvalues only ............
call tred1(nm,n,a,w,fv1,fv2)
call tqlrat(n,w,fv2,ierr)
go to 50

............ find both eigenvalues and eigenvectors ............
20 call tred2(nm,n,a,w,fv1,z)
call tql2(nm,n,w,fv1,z,ierr)
50 return
end
* subroutine tql2(nm,n,d,e,z,ierr)

integer i,j,k,l,m,n,ii,11,12,nm,mnl,ierr
real d(n),e(n),z(nm,n)
real b,c,c2,c3,dl1,el1,f,g,h,p,r,s,s2
real pythag

*** first executable statement tql2
ierr = 0
if (n .eq. 1) go to 1001

do 100 i = 2, n
   100 e(i-1) = e(i)

f = 0.0e0
b = 0.0e0
e(n) = 0.0e0

do 240 l = 1, n
   j = 0
   h = abs(d(l)) + abs(e(l))
   if (b .lt. h) b = h
   ......... look for small sub-diagonal element .........
   do 110 m = 1, n
      if (b + abs(e(m)) .eq. b) go to 120
   end do
   ......... e(n) is always zero, so there is no exit
   through the bottom of the loop .........
   110 continue
   ......... form shift .........
   ll = l + 1
   l2 = ll + 1
   g = d(l)
   p = (d(l1) - g) / (2.0e0 * e(l))
   r = pythag(p,1.0e0)
   d(l) = e(l) / (p + sign(r,p))
   d(ll) = e(l) * (p + sign(r,p))
   dl1 = d(ll)
   h = g - d(l)
   if (l2 .gt. n) go to 145
   do 140 i = ll, n
      140 d(i) = d(i) - h
   end do
   f = f + h
   ......... ql transformation .........
   p = d(m)
c = 1.0e0
c2 = c
e11 = e(11)
s = 0.0e0
ml = m - 1

c ........... for i=m-1 step -1 until 1 do -- ...........
do 200 ii = 1, ml
   c3 = c2
c2 = c
s2 = s
i = m - ii
g = c * e(i)
h = c * p
   if (abs(p) .lt. abs(e(i))) go to 150
   c = e(i) / p
   r = sqrt(c*c+1.0e0)
e(i+1) = s * p * r
   s = c / r
   c = 1.0e0 / r
go to 160
150  c = p / e(i)
r = sqrt(c*c+1.0e0)
e(i+1) = s * e(i) * r
   s = 1.0e0 / r
   c = c * s
160  p = c * d(i) - s * g
    d(i+1) = h + s * (c * g + s * d(i))
c ........... form vector ...........
do 180 k = 1, n
   h = z(k,i+1)
   z(k,i+1) = s * z(k,i) + c * h
   z(k,i) = c * z(k,i) - s * h
180  continue

c 200  continue

c  p = -s * s2 * c3 * e11 * e(1) / d11
e(1) = s * p
d(1) = c * p
   if (b + abs(e(1)).gt. b) go to 130
220  d(1) = d(1) + f
240  continue
c ........... order eigenvalues and eigenvectors ...........
do 300 ii = 2, n
   i = ii - 1
   k = i
   p = d(i)
c
   do 260 j = ii, n
      if (d(j).ge. p) go to 260
   k = j
p = d(j)
continue

if (k .eq. i) go to 300
d(k) = d(i)
d(i) = p

do 280 j = 1, n
   p = z(j,i)
z(j,i) = z(j,k)
z(j,k) = p
280 continue

300 continue

go to 1001

............ set error -- no convergence to an
eigenvalue after 30 iterations ...........

1000 ierr = 1
1001 return

end

subroutine tqlrat(n,d,e2,ierr)

integer i,j,l,m,n,ii,ll,mml,ierr
real d(n),e2(n)
real b,c,f,g,h,p,r,s,machep
real pythag

data machep/1.0e0/
c***first executable statement tqlrat
   if (machep .ne. 1.0e0) go to 10

c   --- this code fails to compute machep correctly on ibm machines. ---
c   --- replaced by call to r1mach on 15 jun 94 by ron boisvert. ---
c
   05 machep = 0.5e0*machep
c   if (1.0e0 + machep .gt. 1.0e0) go to 05
c     machep = 2.0e0*machep
   *
c     machep = r1mach(4)

c
   10 ierr = 0
   if (n .eq. 1) go to 1001

do 100 i = 2, n
100  e2(i-1) = e2(i)

c   f = 0.0e0
   b = 0.0e0
e2(n) = 0.0e0
c
    do 290 l = 1, n
    j = 0
    h = machep * (abs(d(l)) + sqrt(e2(l)))
    if (b .gt. h) go to 105
    b = h
    c = b * b
    c ............ look for small squared sub-diagonal element ...........
    105 do 110 m = 1, n
      if (e2(m) .le. c) go to 120
    c ............ e2(n) is always zero, so there is no exit
    c through the bottom of the loop ...........
    110 continue
    c
    120 if (m .eq. l) go to 210
    130 if (j .eq. 30) go to 1000
    j = j + 1
    c ............ form shift ...........
    ll = l + 1
    s = sqrt(e2(l))
    g = d(l)
    p = (d(ll) - g) / (2.0e0 * s)
    r = pythag(p, 1.0e0)
    d(l) = s / (p + sign(r, p))
    h = g - d(l)
    c
    do 140 i = ll, n
    140 d(i) = d(i) - h
    c
    f = f + h
    c ............ rational ql transformation ...........
    g = d(m)
    if (g .eq. 0.0e0) g = b
    h = g
    s = 0.0e0
    mml = m - l
    c ............ for i=m-1 step -1 until l do -- ...........
    do 200 ii = 1, mml
      i = m - ii
      p = g * h
      r = p + e2(i)
      e2(i+1) = s * r
      s = e2(i) / r
      d(i+1) = h + s * (h + d(i))
      g = d(i) - e2(i) / g
      if (g .eq. 0.0e0) g = b
      h = g * p / r
    200 continue
    c
    e2(l) = s * g
    d(l) = h
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do 150 k = 1, l
    a(i,k) = a(i,k) / scale
    h = h + a(i,k) * a(i,k)
150 continue

c
    e2(i) = scale * scale * h
    f = a(i,l)
    g = -sign(sqrt(h),f)
    e(i) = scale * g
    h = h - f * g
    a(i,l) = f - g
    if (l .eq. l) go to 270
    f = 0.0e0

c
    do 240 j = 1, l
       g = 0.0e0
240    ........... form element of a*u ...........
    do 180 k = 1, j
       g = g + a(j,k) * a(i,k)
180    c
       jpl = j + 1
       if (l .lt. jpl) go to 220
       c
    do 200 k = jpl, l
       g = g + a(k,j) * a(i,k)
200    c
       ........... form element of p ...........
    220    e(j) = g / h
       f = f + e(j) * a(i,j)
    240 continue

c
    h = f / (h + h)

c
    ........... form reduced a ...........
    do 260 j = 1, l
       f = a(i,j)
       g = e(j) - h * f
       e(j) = g
260    c
    do 260 k = 1, j
       a(j,k) = a(j,k) - f * e(k) - g * a(i,k)
260 continue

c
    270 do 280 k = 1, l
    280    a(i,k) = scale * a(i,k)

c
    290    h = d(i)
    d(i) = a(i,i)
    a(i,i) = h
300 continue

c
    return
end
* subroutine tred2(nm,n,a,d,e,z)
  integer i,j,k,l,n,ii,nm,jpl
  real a(nm,n),d(n),e(n),z(nm,n)
  real f,g,h,hh,sscale

  **first executable statement** tred2
  do 100 i = 1, n
  
  do 100 j = 1, i
    z(i,j) = a(i,j)
  100 continue

  if (n .eq. 1) go to 320
  
  do 300 ii = 2, n
    i = n + 2 - ii
    l = i - 1
    h = 0.0e0
    scale = 0.0e0
    if (l .lt. 2) go to 130
  
  do 120 k = 1, l
  120 scale = scale + abs(z(i,k))

  if (scale .ne. 0.0e0) go to 140
  
  e(i) = z(i,l)
  go to 290

  do 150 k = 1, l
    z(i,k) = z(i,k) / scale
    h = h + z(i,k) * z(i,k)
  150 continue

  f = z(i,l)
  g = -sign(sqrt(h),f)
  e(i) = scale * g
  h = h - f * g
  z(i,l) = f - g
  f = 0.0e0

  do 240 j = 1, l
    z(j,i) = z(i,j) / h
    g = 0.0e0
  240 continue

  do 180 k = 1, j
    g = g + z(j,k) * z(i,k)
  180 continue

  if (l .lt. jpl) go to 220
c
   do 200 k = jpl, 1
200   g = g + z(k,j) * z(i,k)
c       ............ form element of p ............
   e(j) = g / h
   f = f + e(j) * z(i,j)
   continue

   hh = f / (h + h)
c       ............ form reduced a ............
   do 260 j = 1, 1
   f = z(i,j)
   g = e(j) - hh * f
   e(j) = g
   continue
   do 260 k = 1, j
   z(j,k) = z(j,k) - f * e(k) - g * z(i,k)
260   continue

   d(i) = h
300   continue

320   d(1) = 0.0e0
   e(1) = 0.0e0
c       ............ accumulation of transformation matrices ............
   do 500 i = 1, n
   l = i - 1
   if (d(i) .eq. 0.0e0) go to 380
   continue
   do 360 j = 1, 1
   g = 0.0e0
   do 340 k = 1, 1
   340   g = g + z(i,k) * z(k,j)
c       do 360 k = 1, 1
   z(k,j) = z(k,j) - g * z(k,i)
360   continue
   do 380 k = 1, 1
   d(i) = z(i,i)
   z(i,i) = 1.0e0
   if (l .lt. 1) go to 500
   do 400 j = 1, 1
   z(i,j) = 0.0e0
   z(j,i) = 0.0e0
400   continue
500   continue

   return
end
*
real function pythag(a,b)
c***begin prologue pythag
c***refer to eisdoc
c
  finds sqrt(a**2+b**2) without overflow or destructive underflow
  routines called (none)
c***end prologue pythag
  real a,b
c
  real p,q,r,s,t
c***first executable statement pythag
    p = amax1(abs(a),abs(b))
    q = amin1(abs(a),abs(b))
    if (q .eq. 0.0e0) go to 20
      10 continue
        r = (q/p)**2
        t = 4.0e0 + r
        if (t .eq. 4.0e0) go to 20
        s = r/t
        p = p + 2.0e0*p*s
        q = q*s
        go to 10
      20 pythag = p
      return
end
Appendix B

The following nonlinear least squares reconstruction routine was developed and used for this application because it provided sufficient accuracy with the a priori knowledge known about the crystal growth process with minimal computational time. Appendix B, begins with a brief review of the mathematics involved with the reconstruction algorithm and a sample of the algorithm used.

The following is taken from *Numerical Recipes: The Art of Scientific Computing (Fortran).*¹ We must consider fitting a model which depends nonlinearly on the set of $M$ unknown parameters $a_k$, $k = 1,2,...,M$. We define a $\chi^2$ merit function and determine best-fit parameters by its minimization. With nonlinear dependencies, however, the minimization must proceed iteratively. Given trial values for the parameters, we develop a procedure that improves the trial solution. The procedure is then repeated until $\chi^2$ stops (or effectively stops) decreasing.

The $\chi^2$ function can be well approximated by a quadratic form, which can be written as

$$\chi^2(a) = \gamma - d \cdot a + \frac{1}{2} a \cdot D \cdot a \quad (B.1)$$

---

where \( \mathbf{d} \) is an \( M \)-vector and \( \mathbf{D} \) is an \( M \times M \) matrix. If the approximation is a good one, we know how to jump from the current trial parameters \( \mathbf{a}_{\text{cur}} \) to the minimizing ones \( \mathbf{a}_{\text{min}} \) in a single leap, namely

\[
\mathbf{a}_{\text{min}} = \mathbf{a}_{\text{cur}} + \mathbf{D}^{-1} \cdot [-\nabla \chi^2(\mathbf{a}_{\text{cur}})]
\]  

(B.2)

On the other hand Eqn. (B.1) might be a poor local approximation to the shape of the function that we are trying to minimize at \( \mathbf{a}_{\text{cur}} \). In that case, about all we can do is take a step down the gradient, as in the steepest descent method. In other words,

\[
\mathbf{a}_{\text{next}} = \mathbf{a}_{\text{cur}} - \text{constant} \times -\nabla \chi^2(\mathbf{a}_{\text{cur}})
\]  

(B.3)

where the constant is small enough not to exhaust the downhill direction.

To use Eqn. (B.2) or Eqn. (B.3), we must be able to compute the gradient of the \( \chi^2 \) function at any set of parameters \( \mathbf{a} \). To use Eqn. (B.2) we also need the matrix \( \mathbf{D} \), which is the second derivative matrix (Hessian matrix) of the \( \chi^2 \) merit function, at any \( \mathbf{a} \). We know exactly the form of \( \chi^2 \), since it is based on a known model function that we have specified. Therefore, the Hessian matrix is known to us.

**B.1 Calculation of the Gradient and Hessian**

The model to be fitted is

\[
y = y(x; \mathbf{a})
\]  

(B.4)

and the \( \chi^2 \) merit function is

\[
\chi^2(\mathbf{a}) = \sum_{i=1}^{N} \left[ \frac{y_i - y(x_i; \mathbf{a})}{\sigma_i} \right]^2.
\]  

(B.5)
The gradient of $\chi^2$ with respect to the parameters $\mathbf{a}$, which will be zero at the $\chi^2$ minimum, has components

$$\frac{\partial \chi^2}{\partial a_k} = -2 \sum_{i=1}^{N} \frac{[y_i - y(x_i; \mathbf{a})]}{\sigma_i^2} \frac{\partial y(x_i; \mathbf{a})}{\partial a_k} \quad k = 1, 2, \ldots, M. \quad (B.6)$$

Taking an additional partial derivative gives

$$\frac{\partial^2 \chi^2}{\partial a_k \partial a_l} = 2 \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \left[ \frac{\partial y(x_i; \mathbf{a})}{\partial a_k} \frac{\partial y(x_i; \mathbf{a})}{\partial a_l} - [y_i - y(x_i; \mathbf{a})] \frac{\partial^2 y(x_i; \mathbf{a})}{\partial a_k \partial a_l} \right]. \quad (B.7)$$

It is conventional to remove the factors of 2 by defining

$$\beta_k = -\frac{1}{2} \frac{\partial \chi^2}{\partial a_k} \quad \alpha_{kl} = \frac{1}{2} \frac{\partial^2 \chi^2}{\partial a_k \partial a_l} \quad (B.8)$$

making $[\alpha] = (1/2) D$ in Eqn. (B.2), in terms of which that equation can be rewritten as the set of linear equations

$$\sum_{i=1}^{M} \alpha_{kl} \delta a_l = \beta_k. \quad (B.9)$$

This set is solved for the increments $\delta a_l$ that, added to the current approximation, give the next approximation. In the context of least-squares, the matrix $[\alpha]$, equal to one-half times the Hessian matrix, is usually called the curvature matrix.

Eqn. (B.3), the steepest descent formula, translates to

$$\delta a_l = \text{constant} \times \beta_l. \quad (B.10)$$
Note that the components $\alpha_{kl}$ of the Hessian matrix, Eqn. (B.7), depends both on the first derivatives and on the second derivatives of the basis function with respect to their parameters.

Second derivatives occur because the gradient Eqn. (B.6) already has a dependence on $\partial y/\partial a_k$, so the next derivative simply must contain terms involving $(\partial^2 y)/\partial a_i \partial a_k$. The second derivative term can be dismissed when it is zero, or small enough to be negligible when compared to the term involving the first derivative. It also has an additional possibility of being ignobly small in practice: The term multiplying the second derivative in Eqn. (B.7) is $[y_i - y(x_i; a)]$. For a successful model, this term should be just a random measurement error of each point. This error can have either sign, and should in general be uncorrelated with the model. Therefore, the second derivative terms tend to cancel out when summed over $i$.

**B.2 Levenberg-Marquardt Method**

Marquardt\(^1\) has put forth an elegant method, related to an earlier suggestion of Levenberg, for varying smoothly between the extremes of the inverse-Hessian method, Eqn. (B.9), and the steepest descent method, Eqn. (B.10). The latter method is used far from the minimum, switching continuously to former as the minimum is approached. This *Levenberg-Marquardt method* (also called the *Marquardt method*) works very well in practice and has become the standard on nonlinear least-squares routines.

The quantity $\chi^2$ is nondimensional, i.e. is a pure number; this is evident from its definition, Eqn. (B.5). On the other hand $\beta_k$ has dimensions of $1/a_k$, which may well be dimensional. The constant of proportionality between $\beta_k$ and $\delta a_k$ must therefore have the dimensions of $a_k^2$. Scan the components of $[\alpha]$ and you see that there is only one obvious

quantity with these dimensions, and that is \(1/\alpha_{kk}\), the reciprocal of the diagonal element. So that must be the scale of the constant. But that scale might itself be too big. So let's divide the constant by some (nondimensional) fudge factor \(\lambda\), with the possibility of setting \(\lambda \rightarrow 1\) to cut down the step. In other words, replace Eqn. (B.10) by

\[
\delta a_l = \frac{1}{\lambda\alpha_{ll}} \beta_l \quad \text{or} \quad \lambda\alpha_{ll}\delta a_l = \beta_l \quad \text{(B.11)}
\]

Marquardt's second insight is that Eqn. (B.11) and Eqn. (B.9) can be combined if we define a new matrix \(\alpha'\) by the following prescription

\[
\alpha'_{jj} = \alpha_{jj}(1 + \lambda) \quad \text{and} \quad \alpha'_{jk} = \alpha_{jk} \quad (j \neq k) \quad \text{(B.12)}
\]

and then replace both Eqn. (B.11) and Eqn. (B.9) by

\[
\sum_{l=1}^{M} \alpha'_{kl}\delta a_l = \beta_k \quad \text{(B.13)}
\]

When \(\lambda\) is very large, the matrix \(\alpha'\) is forced into being diagonally dominant, so Eqn. (B.13) goes over to be identical to Eqn. (B.11). On the other hand, as \(\lambda\) approaches zero, Eqn. (B.13) goes over to Eqn. (B.9).

Given an initial guess for the set of fitted parameters \(a\), the recommended Marquardt recipe is as follows:

- Compute \(\chi^2(a)\).
- Pick a modest value for \(\lambda\), say \(\lambda = 0.001\).
- (†) Solve the linear Eqn. (B.13) for \(\delta a\) and evaluate \(\chi^2(a + \delta a)\).
- If \(\chi^2(a + \delta a) \geq \chi^2(a)\), increase \(\lambda\) by a factor of 10 (or any other substantial factor and go back to (†)).
- If \(\chi^2(a + \delta a) < \chi^2(a)\), decrease \(\lambda\) by a factor of 10, update the trial solution \(a \leftarrow a + \delta a\), and go back to (†).
Also necessary is a condition for stopping. Iterating to convergence is generally wasteful and unnecessary since the minimum is at best only a statistical estimate of the parameters $a$. A change in the parameters that changes $\chi^2$ by an amount $\ll 1$ is never statistically meaningful.

**B.3 Nonlinear Reconstruction Algorithm**

The routine `mrqmin` performs one iteration of Marquardt's method. It is first called (once) with $\lambda < 0$, which signals the routine to initialize. $\lambda$ is returned on the first and all subsequent calls as the suggested value of $\lambda$ for the next iteration; $a$ and $\text{chisq}$ are always returned as the next parameters found so far their $\chi^2$. When convergence is deemed satisfactory, set $\lambda$ to zero before a final call. The matrices $\alpha$ and `covar` (which are used as workspace in all previous calls) will then be set to the curvature and covariance matrices for the converged parameter values. The argument $\alpha$, $a$ and `chisq` must not be modified between calls, nor should $\lambda$ be, except to set it to zero for the final call. When an uphill step is taken, `chisq` and $a$ are returned with their input (best) values, but $\lambda$ is returned with an increased value.

The routine `mrqmin` calls the routine `mrqcof` for the computation of the matrix $[\alpha]$ and vector $\beta$. In turn `mrqcof` calls the user-supplied routine `func`($x, a, y, dyda$), which for input values $x = x_i$ and $a = a$ returns the model function $y = y(x_i; a)$ and the vector of derivatives $dyda = \partial y / \partial a_k$. 

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program convexliq
*
******************************************************************************
* program to fit a series of data points to the best fit equation using a non linear least squares method
* <<numerical recipes example p.150>>
******************************************************************************
*
common /a/ sl,sp,ys,drc
dimension yr(100),t(100)
dimension a(4),lista(20),covar(20,20),alpha(20,20),gues(4)
*
open(30,file='h2liq05inb.dat')
open(40,file='h2liq05outb.dat')
*
write(40,*)'Convex interface, source in solid, h=10mm, zs=-20mm'
write(40,*)
*
read(30,*) sl,rc,sp,ys
write(40,500) sl
500 format ('tube radius: ',f8.2)
write(40,501) rc
501 format ('interface radius of curvature: ',f8.2)
write(40,502) sp
502 format ('solid cylinder radius: ',f8.2)
write(40,503) ys
503 format ('z-axis (source): ',f8.2)
read(30,*) npt,ma,nit
write(40,*)
write(40,*) 'total # of data points: ',npt
write(40,*) 'number of unknown parameters: ',ma
write(40,*) 'maximum # of iterations: ',nit
write(40,*)
*
write(40,*) 'original data'
write(40,*)
do 1 i=1,npt
   read(30,*) yr(i),t(i)
   write(40,504) yr(i),t(i)
504 format ('source point: ',f6.2,'; time-of-flight: ',f6.2)
1 continue
*
   pi = acos(-1.0)
write(40,*)
read(30,*) (gues(i),i=1,ma),drc,alalmda
write(40,505) gues(1)
505 format ('initial guess for interface radius: ',f8.3)
write(40,506) gues(2)
506 format ('initial guess for liquid velocity: ',f8.4)
write(40,507) gues(3)
507  format ('initial guess for solid velocity: ',f8.4)
write(40,508) gues(4)
508  format ('initial guess for originz: ',f10.4)
write(40,'*)
*  
do 15 i=1,ma
15   a(i) = gues(i)
*  
alamda=-1
mfit = ma
do 13 i=1,mfit
    lista(i) = i
13  continue
*  
k = 1
*  
call mrqmin(npt,a,ma,lista,mfit, covar, alpha, chisq, alamda, yr, t)
   istst=0
2000 write(40,'*)
h = (2.*a(1) - sqrt(4.*a(1)**2 - 4.*sp**2))/2
pos0 = (a(1) - h) + a(4)
write(40,'(1x,a,i2,t18,a,f10.4,t43,a,e9.2)')'iteration #',k,
+ 'chi-squared: ',chisq,'alamda: ',alamda
write(40,'*)
write(40,509) h

509  format ('interface height: ',f8.3)
write(40,510) a(2)
510  format ('liquid velocity: ',f8.4)
write(40,511) a(3)
511  format ('solid velocity: ',f8.4)
write(40,512) pos0
512  format ('originz: ',f8.4)
write(40,'*)
*  
k=k+1
 ochisq=chisq
   call mrqmin(npt,a,ma,lista,mfit, covar, alpha, chisq, alamda, yr, t)
if (chisq .gt. ochisq) then
    istst=0
else if (abs(chisq-ochisq) .lt. 0.1) then
   istst=istst+1
end if
*  
if (istst .lt. nit) then
   write(40,'*) 'istst = ',istst,' nit = ',nit
   write(40,'*) '# tests < # iteration, go on'
   write(40,'*)
goto 2000
else
   write(40,'*)
write(40,*) 'itst = ',itst,' nit = ',nit
write(40,*) '# tests = # iteration, run last time'
end if

alamda=0.0
call mrqmin(npt,a,ma,lista,mfit,covar,alpha,chiq,alamda,yr,t)
write(40,*) 'uncertainties'
write(40,'(1x,6f8.4/))' (sqrt(covar(i,i)),i=1,6)
stop
eend

*****************************************************************************
subroutine funct1*****************************************************************************
* subroutine to return if values are possible *
* derivative of partial functions *
*****************************************************************************

subroutine funct1 (yr,p,a,y,dyda,na)
*common /a/ sl,sp,ys,drc
dimension a(*),b(4),c(4),dyda(*)
*
pi = acos(-1.)
xs = -sl
*
do 10 i=1,na
10   if (a(i) .lt. 0.0) a(i) = -a(i)
*
100  if (a(1) .lt. sp) then
      a(1) = a(1) + 10.0
      goto 100
  end if
*
200  if (a(2) .gt. a(3)) then
      a(2) = a(2) - 1.0
      goto 200
  end if
*
  height = (2.*a(1) - sqrt(4.*a(1)**2 - 4.*sp**2))/2.
300  check = (a(1) - height) + a(4)
  if (check .gt. 1.) then
      a(4) = a(4) - 1.0
      goto 300
  end if
  if (check .lt. -1.) then
      a(4) = a(4) + 1.0
      goto 300
  end if
*
call raytra (xs,yr,a,x1,y1,x2,y2,y)
height = (2.*a(1) - sqrt(4.*a(1)**2 - 4.*sp**2))/2.
pos0 = (a(1) - height) + a(4)
if (yr .gt. pos0) then
  sy = sqrt((xs - x1)**2 + (ys - y1)**2) +
      sqrt((sl - x2)**2 + (yr - y2)**2)
else
  sy = sqrt((xs - x1)**2 + (ys - y1)**2)
end if

dyda(2) = -sy/a(2)**2

dyda(3) = -sqrt((x2 - x1)**2 + (y2 - y1)**2)/a(3)**2

* b(1) = a(1) + drc
b(2) = a(2)
b(3) = a(3)
b(4) = a(4)
call raytra (xs, yr, b, x3, y3, x4, y4, z)
dyda(1) = (z - y)/drc

* c(1) = a(1)
c(2) = a(2)
c(3) = a(3)
c(4) = a(4) + drc
call raytra (xs, yr, c, x5, y5, x6, y6, w)
dyda(4) = (w - y)/drc
return
end

******************************************************************************
subroutine raytra******************************************************************************
subroutine to return the minimum time of flight for a horizontal ray path model
******************************************************************************

subroutine raytra(xs, yr, a, x1, y1, x2, y2, t)
common /a/ sl, sp, ys, drc

dimension a(*)

pi = acos(-1.)
radcurv = a(1)
veliq = a(2)
velsol = a(3)
originz = a(4)
t = 0.0

top = 60.0
bottom = -40.0
radchrg = sp
originx = 0.0
sourcey = xs
tolerance = 1000.
endfin = yr

height = (2.*radcurv - sqrt(4.*radcurv**2 - 4.*radchrg**2))/2
pos0 = (radcurv - height) + originz
start = 127.
finish = 145.
step = 0.001

* if (endfin .gt. 0.) then
  do 10 pp = start,finish,step
    ang = pp*(pi/180.)
    tempb = ys - (originx - xs)*tan(ang - pi/2.)
    tempm = (tempb - ys)/(originx - xs)
    asdx = 1.*(1.*originz*tempm**2 - 1.*tempb*tempm**2 +
     0.5*sqrt(-4.*originz**2*tempm**2 +
     4.*radcurv**2*tempm**2 +
     9.*originz*tempb*tempm**2 -
     4.*tempb**2*tempm**2 +
     4.*radcurv**2*tempm**4))/(1.*tempm + tempm**3)
    asdz = 0.5*(2.*tempb + 2.*originz*tempm**2 +
     sqrt(-4.*originz**2*tempm**2 +
     4.*radcurv**2*tempm**2 +
     8.*originz*tempb*tempm**2 -
     4.*tempb**2*tempm**2 +
     4.*radcurv**2*tempm**4))/(1. + tempm**2)
    beta3 = atan((originx - asdx)/(originz - asdz))
    beta4 = atan((asdx - xs)/(ys - asdz))
    qilang = beta3 + beta4
    qilcrit = asin(velliq/velsol)
    if (qilang .lt. qilcrit) then
      solang = asin((velsol/velliq)*sin(qilang))
      beta5 = pi - solang + beta3
      beta6 = pi/2. - beta5
      tempend = tan(betad6)*(radchrq - asdx) + asdz
      if (tempend .gt. pos0 .and. tempend .lt. top) then
        tempb = asdx + tan(betad6)*(originx - asdx)
        tempm = (tempb - asdz)/(originx - asdx)
      if (tempm .gt. 0.0) then
        asd2x = 1.*(1.*originz*tempm**2 - 1.*tempb*tempm**2 +
         0.5*sqrt(-4.*originz**2*tempm**2 +
         4.*radcurv**2*tempm**2 +
         9.*originz*tempb*tempm**2 -
         4.*tempb**2*tempm**2 +
         4.*radcurv**2*tempm**4))/(1.*tempm + tempm**3)
        asd2z = 0.5*(2.*tempb + 2.*originz*tempm**2 +
         sqrt(-4.*originz**2*tempm**2 +
         4.*radcurv**2*tempm**2 +
         8.*originz*tempb*tempm**2 -
         4.*tempb**2*tempm**2 +
         4.*radcurv**2*tempm**4))/(1. + tempm**2)
      else
        asd2x = 1.*(1.*originz*tempm**2 - 1.*tempb*tempm**2 -
         0.5*sqrt(-4.*originz**2*tempm**2 +
         4.*radcurv**2*tempm**2 +
         9.*originz*tempb*tempm**2 -
         4.*tempb**2*tempm**2 +
         4.*radcurv**2*tempm**4))/(1. + tempm**2)
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- 4.*tempb**2*tempm**2 + 
- 4.*radcurv**2*tempm**4))/(1. + tempm**2)

beta3 = atan((originx - asdx)/(originx - asdz))
beta4 = atan((asdx - xs)/(ys - asdz))
qilang = beta3 + beta4
qilcrit = asin(velliq/velsol)
if (qilang .lt. qilcrit) then
    solang = asin((velsol/velliq)*sin(qilang))
    beta5 = pi - solang + beta3
    beta6 = pi/2. - beta5
    tempend = tan(beta6)*(radchrg - asdx) + asdz
if (tempend .gt. bottom .and. tempend .lt. pos0) then
    check = tempend - endfin
    if (abs(check) .lt. tolerance) then
        raya = sqrt((asdx - xs)**2 + (ys - asdz)**2)
tofa = raya/velliq
rayb = sqrt((sp - asdx)**2 + (asdz - tempend)**2)
tofb = rayb/velsol
x1 = asdx
y1 = asdz
x2 = sp
y2 = tempend
t = tofa + tofb + 0.538
tolerance = abs(check)
end if
end if
end if
30 continue
return
end if
end

***********************************************************************
* subroutine mrgmin***********************************************************************
* subroutine using the levenberg-marquardt method
* to reduce the value of chi squared of a fit between
* a set of data and a non-linear function
* <-numerical recipies p.526>
* 
***********************************************************************
* subroutine mrgmin (ndata,a,ma,lista,mfit,covar,alpha,
  + chisq,alamda,yr,p)
* 
  dimension yr(*),a(ma),lista(ma),da(61),
  + covar(ma,*),alpha(ma,*),atry(61),beta(61),p(*)
* 
  initialization
* 
  if (alamda .lt. 0.) then
      kk=mfit+1
*
does lista contain the proper permutation of the coefficients?
*  
    do 12 j=1,ma
       ihit=0
    do 11 k=1,mfit
       if (lista(k) .eq. j) ihit=ihit+1
    11     continue
    if (ihit .eq. 0) then
       lista(kk)=j
       kk=kk+1
    else if (ihit .gt. 1) then
       write (6,*) 'improper permutation in lista'
       stop
    end if
    12     continue
*  
    if (kk .ne. (ma+1)) then
       write (6,*) 'improper permutation in lista'
       stop
    end if
*  
    alama=0.001
    nca = ma
    call mrqcof (ndata,a,ma,lista,mfit,alpha,beta,nca,chisq,
               + yr,p)
    ochisq = chisq
    do 13 j=1,ma
       atry(j)=a(j)
    13    continue
    *  
    alter linearized fitting matrix, by argumenting diagonal
    *  
    elements
    *  
    do 15 j=1,mfit
    do 14 k=1,mfit
       covar(j,k)=alpha(j,k)
    14    continue
    covar(j,j)=alpha(j,j)*(1.+alama)
    da(j)=beta(j)
 15    continue
*  
*  matrix solution
*  
    call gaussj (covar,mfit,nca,da,1,1)
*  
*  once converged evaluate covariance matrix with alama=0
*  
    if (alama .eq. 0.) then
       call covsrt (covar,nca,ma,lista,mfit)
    return
endif

* did the trial succeed?
* do 16 j=1,mfit
   atry(lista(j))=a(lista(j))+da(j)
16 continue
*
call mrqcof (ndata,atry,ma,lista,mfit,covar,da,nca,chisq,
* yr,p)
*
* success, accept the new solution
* if (chisq .lt. ochisq) then
   alamda=0.1*alamda
   ochisq=chisq
*
   do 18 j=1,mfit
      do 17 k=1,mfit
         alpha(j,k)=covar(j,k)
17 continue
   beta(j)=da(j)
   a(lista(j))=atry(lista(j))
18 continue
*
* failure, increase alamda and return
*
else
   alamda=10.*alamda
   chisq=ochisq
endif
*
return
end
*
******************************************************************************
* subroutine mrqcof******************************************************************************
* subroutine for the computation of the matrix alpha and the vector beta
* \<<numerical recipes p.527>>
******************************************************************************
*
subroutine mrqcof (ndata,a,ma,lista,mfit,alpha,beta,nalp,
* + chisq, yr,p)
*
cartoon /a/ s1,sp,ys,dr
cartoon dimension yr(*),p(*)
cartoon dimension alpha(nalp,*), dyda(61),lista(mfit),a(ma),beta(ma)
*
d0 12 j=1,mfit
   do 11 k=1,j

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alpha(j,k)=0.
continue
beta(j)=0.
continue

* summation loop over all data
* chisq=0.
do 15 i=1,ndata
call funct1 (yr(i),p(i),a,ymod,dyda,ma)
dy=p(i)-ymod
do 14 j=1,mfit
   wt=dyda(lista(j))
do 13 k=1,j
   alpha(j,k)=alpha(j,k)+wt*dyda(lista(k))
continue
beta(j)=beta(j)+dy*wt
continue
* find chi squared
* chisq = chisq + dy*dy
continue
do 17 j=2,mfit
* fill in the symmetric side
* do 16 k=1,j-1
   alpha(k,j)=alpha(j,k)
continue
17 continue
end

******************************************************************************
subroutine covsrt******************************************************************************
* subroutine to repack the covar matrix
* to the true order of the parameters
* <<numerical recipies p.515>>
******************************************************************************

subroutine covsrt(covar,ncvm,ma,lista,mfit)

dimension covar(ncvm,ncvm),lista(mfit)
*
zero all elements below diagonal
*
do 12 j = 1,ma-1
   do 11 i = j+1,ma
      covar(i,j) = 0.
continue
12 continue
repack off-diagonal elements to fit into correct
locations below diagonal

do 14 i = 1,mfit-1
   do 13 j = i+1,mfit
      if (lista(j) .gt. lista(i)) then
         covar(lista(j),lista(i)) = covar(i,j)
      else
         covar(lista(i),lista(j)) = covar(i,j)
      end if
13  continue
14  continue

* temporary store original diagonal elements in top row,
and zero the diagonal

swap = covar(1,1)
do 15 j = 1,ma
   covar(1,j) = covar(j,j)
   covar(j,j) = 0.
15  continue

* sort elements into proper order on diagonal

covar(lista(1),lista(1)) = swap
do 16 j = 2,mfit
   covar(lista(j),lista(j)) = covar(1,j)
16  continue

* fill in above diagonal by symmetry

do 18 j = 2,ma
   do 17 i = 1,j-1
      covar(i,j) = covar(j,i)
17  continue
18  continue
return
end

******************************************************************************
* subroutine gaussj*********************************************************
* subroutine to determine the linear equation solution by gauss-jordan *
* <numerical recipies p.28>                                                  *
******************************************************************************
* subroutine gaussj(a,n,mp,b,m,mp)                                        *
* parameter (nmax=50)                                                        *
dimension a(np,np),b(np,mp),ipiv(nmax),indxr(nmax),indxc(nmax)

  do 11 j = 1,n
    ipiv(j) = 0
  11 continue

* main loop over the columns to be reduced
*
  do 22 i = 1,n
    big = 0.
  *
    outer loop of the search for a pivot element
    *
    do 13 j = 1, n
      if (ipiv(j) .ne. 1) then
        do 12 k = 1,n
          if (ipiv(k) .eq. 0) then
            if (abs(a(j,k)) .ge. big) then
              big = abs(a(j,k))
              irow = j
              icol = k
            end if
          else if (ipiv(k) .gt. 1) then
            write(6,'(a)') 'singular matrix, a'
            stop
          end if
        12 continue
      end if
    13 continue

    ipiv(icol) = ipiv(icol) + 1
    *
    if (irow .ne. icol) then
      do 14 l = 1,n
        dum = a(irow,l)
        a(irow,l) = a(icol,l)
        a(icol,l) = dum
      14 continue
    do 15 l = 1,m
      dum = b(irow,l)
      b(irow,l) = b(icol,l)
      b(icol,l) = dum
    15 continue
    end if
    *
    divide the pivot row by the pivot element,
    * located at irow and icol
    *
    indxr(i) = irow
    indxc(i) = icol
    if (a(icol,icol) .eq. 0.) then
write(6,*), 'singular matrix, b'
stop
end if
pivinv = 1./a(icol,icol)
a(icol,icol) = 1.
do 16 l = 1,n
   a(icol,l) = a(icol,l)*pivinv
16 continue
do 17 l = 1,m
   b(icol,l) = b(icol,l)*pivinv
17 continue
*
* reduce the rows, except for the pivot one
* DO 21 ll = 1,n
   IF (ll .NE. icol) THEN
      dum = a(ll,icol)
a(ll,icol) = 0.
do 18 l = 1,n
      a(ll,l) = a(ll,l)-a(icol,l)*dum
18 continue
do 19 l = 1,m
   b(ll,l) = b(ll,l)-b(icol,l)*dum
19 continue
END IF
21 continue
22 continue
*
* unscramble the solution in view of the column interchanges
* DO 24 l = n,1,-1
   IF (indxr(l) .NE. indxc(l)) THEN
      DO 23 k = 1,n
         dum = a(k,indxr(l))
a(k,indxr(l)) = a(k,indxc(l))
a(k,indxc(l)) = dum
23 continue
   END IF
24 continue
RETURN
END