1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

$$c_{ijkl}\frac{\partial^2}{\partial x_l \partial x_j} + \rho F_i = 0.$$

In an isotropic orthonormal medium, this equation, projected on the axis Ox_1, can be written with the aid of relations (1.3.3.5) and (1.3.3.9):

$$c_{11}\frac{\partial^2 u_1}{(\partial x_1)^2} + c_{12}\left[\frac{\partial^2 u_2}{\partial x_1 \partial x_2} + \frac{\partial^2 u_3}{\partial x_1 \partial x_3}\right]$$
$$+ \tfrac{1}{2}(c_{11} - c_{12})\left[\frac{\partial^2 u_1}{(\partial x_2)^2} + \frac{\partial^2 u_3}{\partial x_1 \partial x_3} + \frac{\partial^2 u_1}{(\partial x_3)^2}\right] + \rho F_i$$
$$= 0.$$

This equation can finally be rearranged in one of the three following forms with the aid of Table 1.3.3.3.

$$\tfrac{1}{2}(c_{11} - c_{12})\Delta\mathbf{u} + \tfrac{1}{2}(c_{11} + c_{12})\nabla(\nabla\mathbf{u}) + \rho\mathbf{F} = 0$$
$$\mu\Delta\mathbf{u} + (\mu + \lambda)\nabla(\nabla\mathbf{u}) + \rho\mathbf{F} = 0 \qquad (1.3.3.17)$$
$$\mu\left[\Delta\mathbf{u} + \frac{1}{1 - 2\nu}\nabla(\nabla\mathbf{u})\right] + \rho\mathbf{F} = 0.$$

1.3.4. Propagation of elastic waves in continuous media – dynamic elasticity

1.3.4.1. *Introduction*

The elastic properties of materials have been considered in the preceding section in the static state and the elastic constants have been defined in terms of the response of the material to particular static forces. It is effectively the way the elastic constants have been measured in the past, although the measurements could not be very precise. A way of proceeding frequently used now is to excite a mechanical wave in the crystal and measure its propagation velocity or the wavelength associated with a particular frequency. One method consists in sending a train of ultrasonic waves through the crystal; one uses a pulse generator and a piezoelectric transducer glued to the crystal. The elapsed time between the emission of the train of waves and its reception after reflection from the rear face of the sample is then measured. Another method involves producing a system of standing waves after reflection at the inner surface of the crystal and determining the set of resonance frequencies. The experimental techniques will be described in Section 1.3.4.6.

The purpose of the next sections is to establish relations between the wavelength – or the velocity of propagation – and the elastic constants.

1.3.4.2. *Equation of propagation of a wave in a material*

Consider the propagation of a wave in a continuous medium. The elongation of each point will be of the form

$$\mathbf{u} = \mathbf{u_0}\exp(2\pi i\nu t)\exp(-2\pi i\mathbf{q}\cdot\mathbf{r}), \qquad (1.3.4.1)$$

where ν is the frequency and $\mathbf{q}$ is the wavevector. The velocity of propagation of the wave is

$$V = \nu/q. \qquad (1.3.4.2)$$

We saw in Section 1.3.3.6 that the equilibrium condition is

$$c_{ijkl}\frac{\partial^2 u_k}{\partial x_l \partial x_j} + \rho F_i = 0.$$

Here the only volume forces that we must consider are the inertial forces:

$$c_{ijkl}\frac{\partial^2 u_k}{\partial x_l \partial x_j} = \rho\frac{\partial^2 x_i}{\partial t^2}. \qquad (1.3.4.3)$$

The position vector of the point under consideration is of the form

$$\mathbf{r} = \mathbf{r_0} + \mathbf{u},$$

where only $\mathbf{u}$ depends on the time and $\mathbf{r_0}$ defines the mean position. Equation (1.3.4.3) is written therefore

$$c_{ijkl}\frac{\partial^2 u_k}{\partial x_l \partial x_j} = \rho\frac{\partial^2 u_i}{\partial t^2}. \qquad (1.3.4.4)$$

Replacing $\mathbf{u}$ by its value in (1.3.4.1), dividing by $-4\pi^2$ and using orthonormal coordinates, we get

$$c_{ijkl}u_k q_j q_l = \rho v^2 u_i. \qquad (1.3.4.5)$$

It can be seen that, for a given wavevector, ρv^2 appears as an eigenvalue of the matrix $c_{ijkl}u_k q_j q_l$ of which the vibration vector $\mathbf{u}$ is an eigenvector. This matrix is called the dynamical matrix, or *Christoffel matrix*. In order that the system (1.3.4.5) has a solution other than a trivial one, it is necessary that the associated determinant be equal to zero. It is called the Christoffel determinant and it plays a fundamental role in the study of the propagation of elastic waves in crystals.

Let $\alpha_1, \alpha_2, \alpha_3$ be the direction cosines of the wavevector $\mathbf{q}$. The components of the wavevector are

$$q_i = q\alpha_i.$$

With this relation and (1.3.4.2), the system (1.3.4.5) becomes

$$c_{ijkl}u_k\alpha_j\alpha_l = \rho v^2 u_i. \qquad (1.3.4.6)$$

Putting

$$\Gamma_{ik} = c_{ijkl}\alpha_j\alpha_l \qquad (1.3.4.7)$$

in (1.3.4.6), the condition that the Christoffel determinant is zero can be written

$$\Delta(\Gamma_{ik} - \rho v^2\delta_{ik}) = 0. \qquad (1.3.4.8)$$

On account of the intrinsic symmetry of the tensor of elastic stiffnesses, the matrix Γ_{ik} is symmetrical.

If we introduce into expression (1.3.4.7) the elastic stiffnesses with two indices [equation (1.3.3.6)], we find, for instance, for Γ_{11} and Γ_{12}

$$\Gamma_{11} = c_{11}(\alpha_1)^2 + c_{66}(\alpha_2)^2 + c_{55}(\alpha_3)^2 + 2c_{16}\alpha_1\alpha_2$$
$$+ 2c_{15}\alpha_1\alpha_3 + 2c_{56}\alpha_2\alpha_3$$
$$\Gamma_{12} = c_{16}(\alpha_1)^2 + c_{26}(\alpha_2)^2 + c_{45}(\alpha_3)^2 + (c_{12} + c_{66})\alpha_1\alpha_2$$
$$+ (c_{14} + c_{56})\alpha_1\alpha_3 + (c_{46} + c_{25})\alpha_2\alpha_3.$$

The expression for the effective value, c_{ijkl}^e, of the 'stiffened' elastic stiffness in the case of piezoelectric crystals is given in Section 2.4.2.2.

1.3.4.3. *Dynamic elastic stiffnesses*

Equation (1.3.4.7) may be written

$$\Gamma_{ik} = \sum_{j \neq l}[c_{ijkl} + c_{ilkj}]\alpha_j\alpha_l.$$

This shows that in a dynamic process only the sums $[c_{ijkl} + c_{ilkj}]$ can be measured and not c_{ijkl} and c_{ilkj} separately. On the contrary, c_{ijij} can be measured directly. In the cubic system therefore, for instance, c_{1122} is determined from the measurement

of $[c_{1122} + c_{1221}]$ on the one hand and from that of c_{1221} on the other hand.

1.3.4.4. *Polarization of the elastic waves*

The Christoffel determinant has three roots and the Christoffel matrix, being Hermitian with real coefficients, has three real eigenvalues and three orthogonal eigenvectors. The wavevector **q**, therefore, encompasses three waves with vibration vectors $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_3$ which are perpendicular to one another. In the general case, there is no particular angular relationship between the vibration vectors (or polarization vectors). However, if the latter are parallel to certain symmetry directions in the crystal, one of the vibration vectors is along this direction. The corresponding wave is called longitudinal. The two other waves have their polarization direction perpendicular to the wavevector and are thus transverse. If one of the polarization vectors is almost parallel to the wavevector, which often happens, then one speaks of the vibration as being quasi-longitudinal.

1.3.4.5. *Relation between velocity of propagation and elastic stiffnesses*

We shall limit ourselves to cubic, hexagonal and tetragonal crystals and consider particular cases.

1.3.4.5.1. *Cubic crystals*

(i) *The wavevector is parallel to [100].* The Christoffel determinant reduces to

$$\begin{pmatrix} c_{11} - \rho v^2 & 0 & 0 \\ 0 & c_{44} - \rho v^2 & 0 \\ 0 & 0 & c_{44} - \rho v^2 \end{pmatrix} = 0.$$

The three solutions are given in Table 1.3.4.1. These results are valid for a wave propagating in any direction in an isotropic medium.

(ii) *The wavevector is parallel to [110].* The direction cosines of the wavevector are $1/\sqrt{2}$, $1/\sqrt{2}$, 0. The Christoffel determinant assumes the form

$$\begin{pmatrix} \frac{1}{2}(c_{11} + c_{44}) - \rho v^2 & \frac{1}{2}(c_{12} + c_{44}) & 0 \\ \frac{1}{2}(c_{12} + c_{44}) & \frac{1}{2}(c_{11} + c_{44}) - \rho v^2 & 0 \\ 0 & 0 & c_{44} - \rho v^2 \end{pmatrix} = 0.$$

The three solutions are given in Table 1.3.4.2.

(iii) *The wavevector is parallel to [111].* The Christoffel determinant assumes the form

$$\begin{pmatrix} c_{11} + 2c_{44} - \rho v^2 & c_{12} + c_{44} & c_{12} + c_{44} \\ c_{12} + c_{44} & c_{11} + 2c_{44} - \rho v^2 & c_{12} + c_{44} \\ c_{12} + c_{44} & c_{12} + c_{44} & c_{44} - \rho v^2 \end{pmatrix} = 0.$$

The solutions are given in Table 1.3.4.3.

1.3.4.5.2. *Hexagonal crystals*

In hexagonal crystals, there are five independent elastic stiffnesses, c_{11}, c_{33}, c_{12}, c_{13}, c_{44} and $c_{66} = (c_{11} - c_{12})/2$ (Section 1.1.4.10.4).

(i) *The wavevector is parallel to [001].* The Christoffel determinant reduces to

$$\begin{pmatrix} c_{44} - \rho v^2 & 0 & 0 \\ 0 & c_{44} - \rho v^2 & 0 \\ 0 & 0 & c_{33} - \rho v^2 \end{pmatrix} = 0.$$

The solutions are given in Table 1.3.4.4.

(ii) *The wavevector is parallel to [100].* The Christoffel determinant readily reduces to

$$\begin{pmatrix} c_{11} - \rho v^2 & 0 & 0 \\ 0 & c_{66} - \rho v^2 & 0 \\ 0 & 0 & c_{44} - \rho v^2 \end{pmatrix} = 0.$$

The three solutions are given in Table 1.3.4.5.

1.3.4.5.3. *Tetragonal crystals (classes 4mm, $\bar{4}$2m, 4/mmm)*

In tetragonal crystals, there are six independent elastic stiffnesses, c_{11}, c_{33}, c_{12}, c_{13}, c_{44} and c_{66} (Section 1.1.4.10.4).

(i) *The wavevector is parallel to [001].* The Christoffel determinant reduces to

Table 1.3.4.1. *Velocity of propagation when the wavevector is parallel to [100] (cubic crystals)*

Velocity of propagation	Polarization vector	Nature of the wave
$v_\parallel = \sqrt{c_{11}/\rho}$	[100]	Longitudinal
$v_\perp = \sqrt{c_{44}/\rho}$	[010]	Transverse
$v_\perp = \sqrt{c_{44}/\rho}$	Any vector normal to [100]	Transverse

Table 1.3.4.2. *Velocity of propagation when the wavevector is parallel to [110] (cubic crystals)*

Velocity of propagation	Polarization vector	Nature of the wave
$v_\parallel = \sqrt{[c_{44} + \frac{1}{2}(c_{11} + c_{12})]/\rho}$	[110]	Longitudinal
$v_\perp = \sqrt{\frac{1}{2}(c_{11} - c_{12})/\rho}$	[1$\bar{1}$0]	Transverse
$v_\perp = \sqrt{c_{44}/\rho}$	[001]	Transverse

Table 1.3.4.3. *Velocity of propagation when the wavevector is parallel to [111] (cubic crystals)*

Velocity of propagation	Polarization vector	Nature of the wave
$v_\parallel = \sqrt{(c_{11} + 2c_{12} + 4c_{44})/3\rho}$	[111]	Longitudinal
$v_\perp = \sqrt{(c_{11} - c_{12} + c_{44})/3\rho}$	Any vector normal to [111]	Transverse

Table 1.3.4.4. *Velocity of propagation when the wavevector is parallel to [001] (hexagonal crystals)*

Velocity of propagation	Polarization vector	Nature of the wave
$v_\parallel = \sqrt{c_{33}/\rho}$	[100]	Longitudinal
$v_\perp = \sqrt{c_{44}/\rho}$	Any vector normal to [001]	Transverse

Table 1.3.4.5. *Velocity of propagation when the wavevector is parallel to [100] (hexagonal crystals)*

Velocity of propagation	Polarization vector	Nature of the wave
$v_\parallel = \sqrt{c_{11}/\rho}$	[100]	Longitudinal
$v_\perp = \sqrt{c_{66}/\rho}$	[010]	Transverse
$v_\perp = \sqrt{c_{44}/\rho}$	[001]	Transverse

Table 1.3.4.6. *Velocity of propagation when the wavevector is parallel to [001] (tetragonal crystals)*

Velocity of propagation	Polarization vector	Nature of the wave
$v_\parallel = \sqrt{c_{33}/\rho}$	[100]	Longitudinal
$v_\perp = \sqrt{c_{44}/\rho}$	[010]	Transverse
$v_\perp = \sqrt{c_{44}/\rho}$	[001]	Transverse

Table 1.3.4.7. *Velocity of propagation when the wavevector is parallel to [100] (tetragonal crystals)*

Velocity of propagation	Polarization vector	Nature of the wave
$v_\parallel = \sqrt{c_{11}/\rho}$	[100]	Longitudinal
$v_\perp = \sqrt{c_{66}/\rho}$	[010]	Transverse
$v_\perp = \sqrt{c_{44}/\rho}$	[001]	Transverse

$$\begin{pmatrix} c_{44} - \rho v^2 & 0 & 0 \\ 0 & c_{44} - \rho v^2 & 0 \\ 0 & 0 & c_{33} - \rho v^2 \end{pmatrix} = 0.$$

The three solutions are given in Table 1.3.4.6.

(ii) *The wavevector is parallel to [100]*. The Christoffel determinant reduces to

$$\begin{pmatrix} c_{11} - \rho v^2 & 0 & 0 \\ 0 & c_{66} -^2 \rho v^2 & 0 \\ 0 & 0 & c_{44} -^2 \rho v^2 \end{pmatrix} = 0.$$

The three solutions are given in Table 1.3.4.7.

1.3.4.6. *Experimental determination of elastic constants*

1.3.4.6.1. *Introduction*

As mentioned in Section 1.3.4.1, the elastic constants of a material can be obtained by the elastic response of the material to particular static forces; however, such measurements are not precise and the most often used approach nowadays consists of determining the velocity of ultrasonic waves propagating along different directions of the crystal and calculating the elastic constants from the Christoffel determinants (1.3.4.8). The experimental values are often accurate enough to justify the distinction between static and dynamic values of the elastic constants and between phase and group velocities, and the careful consideration of the frequency range of the experiments.

(i) *Static and dynamic elastic constants*. When one measures the elastic response of a material to external static forces, work is done and heat is produced. In general, the external forces are applied slowly (quasi-elastic processes) and the solid body remains in thermal equilibrium with its surroundings, which can be considered as a heat reservoir. In this case, the measured elastic constants are isothermal elastic constants as defined in Section 1.1.5.1. On the contrary, when ultrasonic waves propagate in a solid body, the compressed regions are slightly hotter than the expanded regions; the associated temperature gradients give rise to irreversible processes of thermal conduction. However, in the megahertz or higher-frequency ranges, the processes of heat exchange between different regions or between the solid and its surroundings are slow compared with the period of the ultrasonic wave and hence can be considered as isentropic. In this case, the measured velocities are isentropic and the elastic stiffnesses deduced from them are the adiabatic elastic stiffnesses as defined in Section 1.1.5.4. The differences between isothermal and adiabatic elastic stiffnesses can be calculated from equation (1.1.5.2):

$$\delta T_{ij} = (c_{ijkl})^\Theta \delta S_{kl} - \lambda_{ij}\delta\Theta$$

$$\delta\sigma = \lambda_{kl}\delta S_{kl} + \frac{\rho C^S}{\Theta}\delta\Theta.$$

By combining these two equations, it is possible to obtain relations between the isothermal elastic stiffnesses, $(c_{ijkl})^\Theta$, and the adiabatic elastic stiffnesses, $(c_{ijkl})^\sigma$:

$$(c_{ijkl})^\sigma = (c_{ijkl})^\Theta + \frac{\lambda_{ij}\lambda_{kl}}{\rho c^S},$$

where c^S is the specific heat at constant strain.

This relation shows that adiabatic elastic stiffnesses are larger than isothermal elastic stiffnesses, at least for the terms of the main diagonal of the elastic matrix. In general, the differences between isothermal and adiabatic elastic stiffnesses are less than 1%. An exception to this statement concerns the temperature region near the critical temperature T_c where a phase transition occurs.

(ii) *Frequency dependence of the elastic constants*. Dynamic measurements of the elastic constants can be performed at a wide range of ultrasonic frequencies. Currently used techniques for investigating a wide range of frequencies are electronic pulse-echo techniques in the megahertz frequency range and Brillouin scattering in the 10 GHz frequency range. To evaluate the possible differences between dynamic elastic constants determined in different frequency ranges, high-accuracy measurements of the *absolute value* of the elastic constants are required. From optical resonance techniques in the megahertz frequency range and Brillouin scattering in the gigahertz frequency range, it has been shown that the results are the same within 0.1 to 0.2% in the case of simple and stable crystals such as sodium chloride when the ultrasonic waves can be considered as a 'passive probe' (Michard *et al.*, 1971). Larger differences are observed when ultrasonic waves interact with the medium, when they favour or impede structural changes of the material or when they are absorbed for a particular frequency.

(iii) *Phase velocity and group velocity*. When the velocity of ultrasonic waves is frequency dependent (dispersive medium), one has to distinguish phase velocity and group velocity. If a resonance technique is used, the resonance frequencies correspond to phase-matching conditions and the calculation of velocity from the resonance frequencies leads to '*phase velocity*'. If a pulse-echo technique is used, the transit time of an elastic pulse is measured and the interpretation of the measurement is more complex. In this case, Brillouin (1932) has shown that the head and the tail of the pulse travel with the group velocity. Differences of a few per cent can be observed between phase and group velocities in dispersive media.

1.3.4.6.2. *Resonance technique*

The use of the resonance technique is a well established approach for determining the velocity of sound in a gas by observing nodes and antinodes of a system of standing waves produced in the so-called *Kund tube*. In the case of transparent solids, optical means allow us to visualize the standing waves and to measure the wavelength directly (Zarembowitch, 1965). An easier procedure can be used: let us consider a transparent crystal in the shape of a parallelepiped (Fig. 1.3.4.1). A piezoelectric transducer is glued to the crystal and excited at varying frequencies. If the bonding between the transducer and the crystal is loose enough, the crystal can be considered as free from stress and the sequence of its resonance frequencies is given by

$$v = nV/2l,$$

where n is an integer, V the phase velocity of the wave in the direction orthogonal to the parallel faces and l the distance between these faces.

The looseness of the bonding can be checked by the regularity of the arithmetic ratio, $V/2l$. On account of the elasto-optic coupling, a phase grating is associated with the elastic standing-wave system and a light beam can be diffracted by this grating. The intensity of the diffraction pattern is maximum when resonance occurs. A large number of resonance frequencies can be detected, usually more than 100, sometimes 1000 for non-attenuating materials. Consequently, in favourable cases the absolute value of the ultrasonic velocity can be determined with an uncertainty less than 10^{-3}.

1.3.4.6.3. *Pulse-echo techniques*

Pulse-echo techniques are valid for transparent and opaque materials. They are currently used for measuring ultrasonic velocities in solids and can be used in very simple as well as in sophisticated versions according to the required precision (McSkimmin, 1964). In the simplest version (Fig. 1.3.4.2), an
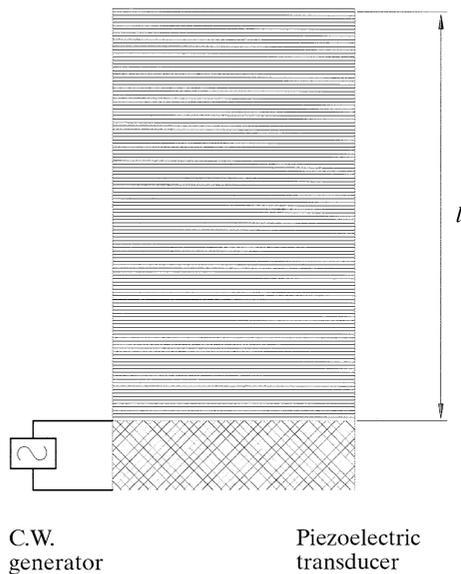
Fig. 1.3.4.1. Resonance technique: standing waves excited in a parallelepiped.

C.W. generator

Piezoelectric transducer

electronic pulse generator excites the mechanical vibrations of a piezo-electric transducer glued to one of two plane-parallel faces of a specimen. An ultrasonic pulse whose duration is of the order of a microsecond is generated and transmitted through the specimen. After reflection at the opposite face, it returns and, when it arrives back at the transducer, it gives rise to an electronic signal, or echo. The whole sequence of such echos is displayed on the screen of an oscilloscope and it is possible to measure from them the time interval for transit. Usually, X-cut quartz crystals or ferroelectric ceramics are used to excite longitudinal waves and Y-cut quartz is used to excite transverse waves. In many cases, a circulator, or gate, is used to protect the receiver from saturation following the main 'bang'. This method is rough because the beginning and the end of a pulse are not well characterized. Several improvements have therefore been made, mainly based on interferometric techniques (pulse-superposition method, 'sing around' method etc.). Nevertheless, if the absolute value of the ultrasonic velocity is not determined with a high accuracy by using pulse-echo techniques, this approach has proved valuable when relative values of ultrasonic velocities are needed, e.g. temperature and pressure dependences of ultrasonic velocities.

(i) *Pulse-superposition method*. A piezoelectric transducer initiates ultrasonic pulses in the specimen. These pulses echo back and forth within the specimen. A continuous-wave oscillator is used to control the pulse repetition rate. When the repetition rate is adjusted so that the initiation of a pulse coincides with the return of the first echo from the preceding pulses, the change in the signal amplitude indicates superposition. The pulse rate is a measure of the travel time within the specimen.

(ii) *'Sing around method'*. The 'sing around' method for measuring the velocity of ultrasonic waves involves the use of two piezoelectric transducers, one at each end of the specimen. One transducer receives an impulse from the electronic generator and converts it into an ultrasonic pulse in the specimen. This pulse, after passing through the specimen, is detected by the receiving transducer. The received pulse triggers the electronic generator to initiate a succeeding pulse. The pulse repetition rate is a very sensitive probe for measuring changes of the ultrasonic velocity in the specimen. Relative variations of 10^{-7} can be measured, such as temperature or stress dependences of the velocity.

1.3.5. Pressure dependence and temperature dependence of the elastic constants

1.3.5.1. *Introduction*

In a solid, the elastic constants are temperature and pressure dependent. As examples, the *temperature dependence* of the elastic stiffnesses of an aluminium single crystal within its stability domain (the melting point is 933 K) and the *pressure dependence* of the elastic stiffnesses of the ternary compound $KZnF_3$ within its stability domain (the crystal becomes unstable for a hydrostatic pressure of about 20 GPa) are shown in Figs. 1.3.5.1 and 1.3.5.2, respectively.

We can observe the following trends, which are general for stable crystals:

(i) From 0 K to about $\Theta_D/5$, where Θ_D is the Debye temperature, the elastic stiffnesses decrease according to a Θ^4 law. From $\Theta_D/5$ to the beginning of the instability domain, the dependence is linear with Θ. In addition, $(\partial c_{ii}/\partial\Theta)_p = 0$ at 0 K as predicted by the third principle of thermodynamics.

(ii) For stable crystals, the *pressure dependence* of the elastic stiffness is linear as long as the applied pressure is small compared to the elastic stiffnesses. As an example, a typical order of magnitude for c_{11} in crystals is about 100 GPa and, within the experimental uncertainty, the pressure dependence of c_{11} does not depart from a linear behaviour up to at least 0.2 GPa.

These observations can be quantitatively justified on the basis of an equation of state of a solid:
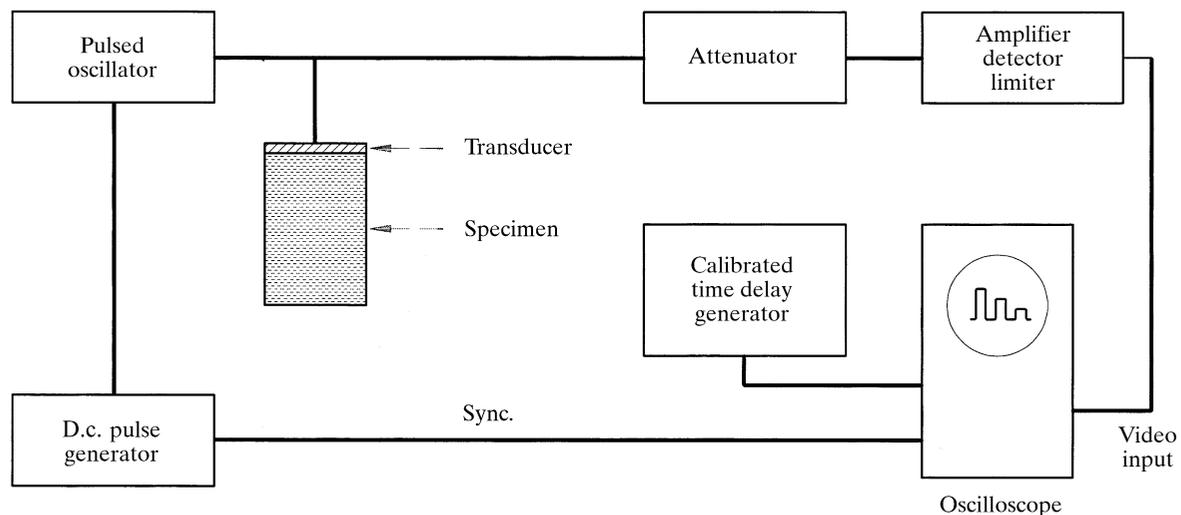
$$f(T_{ij}, S_{ij}, X, \Theta) = 0,$$

Fig. 1.3.4.2. Block diagram of the pulse-echo technique.

Pulsed oscillator

Attenuator

Amplifier detector limiter

Transducer

Specimen

Calibrated time delay generator

D.c. pulse generator

Sync.

Oscilloscope

Video input

references